MINISTRY OF AGRICULTURE AND FISHERIES

TECHNICAL BULLETIN NO. 1

Specifications and Methods of Analysis for certain Insecticides and Fungicides

Compiled by the Plant Pathology Laboratory of the Ministry of Agriculture and Fisheries

1949

LONDON: HIS MAJESTY'S STATIONERY OFFICE

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FOREWORD

THE STANDARDIZATION of insecticides and fungicides has attracted considerable interest in recent years. In 1934 the Association of British Insecticide Manufacturers prepared specifications for certain materials, including the lead arsenates and lime sulphur, and drew up methods of analysis for use with the specifications. The specifications and methods were accepted by the Ministry, the Government Chemist and the manufacturers, and were published by the Ministry in Bulletin No. 82. Later, a joint committee of the Ministry and the Association prepared similar specifications and methods of analysis for the tar oil winter washes; these were officially accepted and were published in Bulletin No. 122. Members of the Association of British Insecticide Manufacturers and other firms agreed that their products should conform to the official specifications. A notable advance was thus made.

Specifications and methods of analysis for additional classes of insecticides and fungicides have now been prepared by other joint committees of the Ministry and the Association. The specifications and methods given in Bulletin No. 82 have also been revised wherever possible, and all are now brought together in this Technical Bulletin, which replaces the two earlier Bulletins. The work has been carried out over a number of years and differences in the expression or description of particular items have inevitably resulted. The specifications and methods, however, have been reproduced as drawn up by the committees.

The specifications and methods have been accepted by the Ministry, the Government Chemist, and the manufacturers, and have been used as the basis for the approval of proprietary products under the Ministry's voluntary approval scheme. The specifications are not intended to be buying specifications for the ingredients used in the compounded materials; they relate solely to the manufactured products. The specifications indicate the minimum standards to which the various insecticides and fungicides should conform, if the materials are to be satisfactory when applied at the rates of dilution normally used. While the specifications take into account as far as is possible at the present time the factors concerned with efficiency, other considerations which cannot be specified, e.g. faulty methods of application or abnormal environmental conditions at the time of application, may play an important part in the effectiveness of the products.

The analytical control of certain materials has presented difficulties and the committees preparing the specifications have found it necessary to undertake detailed investigations and to work out new methods for some of the determinations. It is possible that with further advances in knowledge revision of the specifications and methods may become necessary. Attention will be given later to the important question of detailed recommendations for the sampling of the different types of products. The lack of sufficient information concerning the physical properties required for satisfactory dusts has so far precluded the preparation of specifications for materials applied in powder form, but it is hoped that as a result of further research this difficulty will be overcome.

The membership of the joint committees which have drawn up the specifications and methods is given on pages 5 and 6. The Ministry is greatly indebted to the members of the Research Stations, Government Laboratory and firms who have taken part in the work, and to the Association of British Insecticide Manufacturers for its ready and helpful co-operation. The compilation of this Bulletin has been made by Dr. J. T. Martin of this Laboratory.

C. T. GIMINGHAM.

Plant Pathology Laboratory,
Harpenden, Herts.

February, 1949.

MEMBERSHIP OF THE JOINT COMMITTEES OF THE MINISTRY AND THE ASSOCIATION OF BRITISH INSECTICIDE MANUFACTURERS

Tar Oil Winter Washes

Mr. C. T. Gimingham (*Chairman*)	Ministry of Agriculture and Fisheries
Mr. H. M. Lowe	Dorman, Long & Co. Ltd.
Dr. H. Martin	Long Ashton Research Station
Mr. W. R. Orrell	Plant Protection Ltd.
Dr. H. Shaw	East Malling Research Station
Mr. N. K. Smith	The Murphy Chemical Co. Ltd.
Mr. W. A. Williams (*Secretary*)	Association of British Insecticide Manufacturers

Petroleum Oil Winter Washes, Petroleum Oil Summer Washes and Tar-petroleum Oil Winter Washes

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Mr. E. T. Buggé	Buggé's Insecticides Ltd.
Mr. C. H. Hardy	Shell Chemicals Ltd.
Mr. H. I. Kingston	Geo. Monro Ltd.
Dr. H. Martin	Long Ashton Research Station
Mr. W. R. Orrell	Plant Protection Ltd.
Dr. D. D. Pratt	D.S.I.R. Chemical Research Laboratory
Dr. H. Shaw	East Malling Research Station
Mr. N. K. Smith	The Murphy Chemical Co. Ltd.
Mr. W. A. Williams and Dr. J. T. Martin (*Secretaries*)	Association of British Insecticide Manufacturers; Ministry of Agriculture and Fisheries

Dinitro-*ortho*-cresol-petroleum Oil Winter Washes

Mr. C. T. Gimingham (*Chairman*)	Ministry of Agriculture and Fisheries
Mr. E. T. Buggé	Buggé's Insecticides Ltd.
Mr. C. H. Hardy	Shell Chemicals Ltd.
Dr. H. Martin	Long Ashton Research Station
Mr. W. R. Orrell	Plant Protection Ltd.
Dr. D. D. Pratt	D.S.I.R. Chemical Research Laboratory
Dr. H. Shaw	East Malling Research Station
Mr. N. K. Smith	The Murphy Chemical Co. Ltd.
Dr. R. L. Wain	South-Eastern Agricultural College, Wye
Mr. W. A. Williams and Dr. J. T. Martin (*Secretaries*)	Association of British Insecticide Manufacturers; Ministry of Agriculture and Fisheries

Lime Sulphur Washes

Dr. H. Martin (*Chairman*)	Long Ashton Research Station
Dr. J. R. Booer	F. W. Berk & Co. Ltd.
Mr. E. T. Buggé	Buggé's Insecticides Ltd.
Mr. J. Ramsay Gray	Burt, Boulton & Haywood Ltd.

LIME SULPHUR WASHES—*cont.*

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Mr. W. R. Orrell		Plant Protection Ltd.
Dr. H. Shaw		East Malling Research Station
Dr. J. K. Eaton		East Malling Research Station
Mr. H. W. Vallender and Dr. J. T. Martin	*Secretaries*	Association of British Insecticide Manufacturers; Ministry of Agriculture and Fisheries

LEAD ARSENATE POWDERS AND PASTES

Mr. H. J. Jones (*Chairman*)		Hemingway & Co. Ltd.
Mr. M. FitzGibbon		Lunevale Products Ltd.
Dr. J. R. Nicholls		The Government Laboratory
Dr. H. Shaw		East Malling Research Station
Mr. A. D. Snowden		Blundell Spence & Co. Ltd.
Mr. H. W. Vallender and Dr. J. T. Martin	*Secretaries*	Association of British Insecticide Manufacturers; Ministry of Agriculture and Fisheries

PARIS GREEN

Mr. H. J. Jones (*Chairman*)		Hemingway & Co. Ltd.
Dr. J. R. Nicholls		The Government Laboratory
Dr. H. Shaw		East Malling Research Station
Mr. A. D. Snowden		Blundell Spence & Co. Ltd.
Mr. H. W. Vallender and Dr. J. T. Martin	*Secretaries*	Association of British Insecticide Manufacturers; Ministry of Agriculture and Fisheries

NICOTINE AND NICOTINE SULPHATE

Dr. H. Martin (*Chairman*)		Long Ashton Research Station
Mr. E. J. Cakebread		Pan Britannica Industries Ltd.
Dr. J. R. Nicholls		The Government Laboratory
Dr. J. H. Reid		British Nicotine Co. Ltd.
Mr. H. W. Vallender and Dr. J. T. Martin	*Secretaries*	Association of British Insecticide Manufacturers; Ministry of Agriculture and Fisheries

FORMALDEHYDE AND METALDEHYDE

Dr. H. Martin (*Chairman*)		Long Ashton Research Station
Mr. E. J. Cakebread		Pan Britannica Industries Ltd.
Mr. J. King		The Government Laboratory
Mr. N. Strafford		I.C.I. Ltd., Dyestuffs Division
Mr. H. W. Vallender and Dr. J. T. Martin	*Secretaries*	Association of British Insecticide Manufacturers; Ministry of Agriculture and Fisheries

COPPER SULPHATE

Specification taken from the Ministry's Bulletin No. 82; methods of analysis revised by

Dr. H. Martin		Long Ashton Research Station
Dr. J. R. Nicholls		The Government Laboratory
Dr. J. T. Martin (*Secretary*)		Ministry of Agriculture and Fisheries

Specifications and Methods of Analysis for Certain Insecticides and Fungicides

COPPER SULPHATE

SPECIFICATION

Copper sulphate shall contain not less than 98 per cent of crystallized copper sulphate ($CuSO_4.5H_2O$) when tested by one of the prescribed methods CS 1, CS 2.

METHODS OF ANALYSIS

Determination of Copper Sulphate CS 1

REAGENTS

Concentrated nitric acid
Absolute alcohol or acetone
Sulphuretted hydrogen

APPARATUS

1 stoppered weighing bottle
1 electrolysis apparatus with rotating platinum cathode
1 oven at 100° C.

METHOD

Weigh about 2 g. of the sample, coarsely crushed if necessary, by difference from a stoppered weighing bottle and dissolve in 200 ml. of distilled water. Add 3 ml. of concentrated nitric acid and electrolyse the solution at room temperature, employing a weighed rotating platinum cathode (a gauze cylinder about 2½ cm. long and 2½ cm. diameter is suitable) and a current density of about 0.06 amperes per sq. cm. Continue the electrolysis for half an hour after the solution appears colourless. Wash the cathode with distilled water without stopping the current, disconnect, wash with alcohol or acetone, dry at 100° C. and weigh.

Copper deposited × 3.9282 = cryst. copper sulphate ($CuSO_4.5\,H_2O$).

The complete deposition of the copper should be confirmed by passing sulphuretted hydrogen through the solution; no appreciable darkening should occur.

Determination of Copper Sulphate CS 2

REAGENTS

Electrolytic copper foil
Concentrated nitric acid
Saturated sodium carbonate solution
Acetic acid solution (dilute)
Starch solution
Saturated sodium fluoride solution
Potassium iodide
Sodium thiosulphate solution (0.1 N to 0.2 N)

APPARATUS

2 600 ml. conical flasks
1 10 ml. measuring cylinder
1 100 ml. measuring cylinder
1 stoppered weighing bottle
1 burette

METHOD

(a) *Standardization of Sodium Thiosulphate solution.* Weigh accurately about 0.5 g. of electrolytic copper foil into a 600 ml. flask, add 5 ml. of nitric acid and 5 ml. of water, and evaporate nearly to dryness; cool, add 100 ml. of water and boil; cool, add a slight excess of sodium carbonate solution and then dilute acetic acid until the mixture is slightly acid. Add 10 ml. of saturated sodium fluoride solution, followed by 5 g. of potassium

iodide. Titrate the liberated iodine with sodium thiosulphate solution (0.1 N to 0.2 N) until the yellow colour has nearly disappeared, add a little freshly prepared soluble starch solution and continue the titration until the blue colour disappears. The strength of the sodium thiosulphate solution in terms of crystallized copper sulphate ($CuSO_4.5H_2O$) is given by

$$\frac{\text{Weight of copper taken} \times 3.928}{\text{ml. thiosulphate solution}} \text{ g. per ml.}$$

(b) *Determination of Copper Sulphate in sample.* Weigh accurately about 2 g. of the sample, coarsely crushed if necessary, by difference from a stoppered weighing bottle and dissolve in 100 ml. of water. Add 3 drops of nitric acid, boil and cool. Proceed as described in the standardization of the sodium thiosulphate solution, starting with " add a slight excess of sodium carbonate solution ", until the titration is completed.

The percentage of copper sulphate in the sample is given by

$$\frac{\text{ml. thiosulphate solution} \times \text{strength (g. of } CuSO_4.5H_2O \text{ per ml.)} \times 100}{\text{weight of sample taken}}$$

LIME SULPHUR SOLUTION

SPECIFICATION

The lime sulphur solution shall be clear and free from sludge.

1. *Apparent density.* The solution shall have an apparent density at 20° C. of 1.30 ± 0.01 expressed as g./ml. when determined by the prescribed method LS 1.

2. *Polysulphide Sulphur content.* The solution shall contain not less than 24 per cent weight in volume of polysulphide sulphur when determined by the prescribed method LS 2.

METHODS OF ANALYSIS

Sampling

The sample shall be thoroughly mixed before taking a portion for analysis. Samples should be kept in completely filled, well-stoppered containers.

Determination of Apparent Density LS 1

APPARATUS

Thermometer reading to 0.5° C.

Hydrometer jar of clear glass, cylindrical in form and provided with a lip for convenience in pouring. The diameter of the jar shall be at least 2.5 cm. greater than that of the hydrometer.

Hydrometer conforming to B.S. 718, 1936.

METHOD

Pour the sample to be tested into the clean hydrometer jar so as to avoid the formation of air bubbles. Stand the jar in a vertical position in a place free from air currents.

Lower the hydrometer gently into the sample and when it has settled depress it about two scale divisions into the sample and then release it. When the hydrometer has come to rest, floating freely away from the walls of the jar, take the hydrometer reading at the point where the surface of the liquid cuts the scale. Determine this point by placing the eye slightly below the level of the liquid and raising it until the surface appears to become a straight line cutting the hydrometer scale.

The temperature of the sample immediately before and after the determination of its apparent density shall be 20° C. ± 0.5°.

Determination of Polysulphide Sulphur LS 2

Reagents

Ammoniacal zinc chloride solution. Dissolve 50 g. zinc chloride (pure for analysis) in 500 ml. water, add 125 ml. ammonium hydroxide (A.R., sp. gr. about 0.880), 50 g. ammonium chloride (A.R.), and dilute to 1 litre.

Sodium sulphite solution. Dissolve 25 g. $Na_2SO_3.7H_2O$ (A.R.) in water and make up to 250 ml. Use only the freshly prepared solution.

Strontium chloride solution. Dissolve 100 g. $SrCl_2.6H_2O$ (pure for analysis) in water and make up to 1 litre.

Tartaric acid (freshly prepared 10 per cent solution).

0.05 N iodine solution standardized against arsenious oxide dried at 105° C.

One per cent starch solution.

Methyl red solution (0.2 per cent in 95 per cent alcohol).

Apparatus

1 50 ml. weighing bottle
3 250 ml. graduated flasks
1 350 ml. conical flask
Filter funnel and filter paper
Steam bath
Wash bottle of distilled water
1 50 ml. burette

Method

Transfer about 10 ml. of the sample into a tared 50 ml. weighing bottle; weigh as quickly as possible (w g.) and transfer to a 250 ml. graduated flask. Make up to mark with boiled and cooled distilled water and mix well.

Immediately add 25 ml. of the diluted material to a 350 ml. conical flask containing 10 ml. of the ammoniacal zinc chloride solution and 35 ml. of the sodium sulphite solution. Place the flask on a steam bath at full heat for at least 45 minutes, shaking the flask and washing down the sides with boiling water from a wash bottle at about ten minute intervals. Remove the flask from steam bath.

Add 30 ml. of the strontium chloride solution, allow to stand for five minutes and transfer to a 250 ml. graduated flask. Cool, make up to the mark and shake. Filter through a dry filter paper of diameter not greater than 12.5 cm. rejecting the first portion of the filtrate until clear. To a 50 ml. aliquot of the filtrate add one drop of methyl red solution and titrate to slight acidity with the tartaric acid solution. Titrate using starch as indicator with 0.05 N iodine solution (x ml.).

Correction for Thiosulphate content

The figure obtained must be corrected for the thiosulphate sulphur content originally present. This correction is obtained as follows:

Add 25 ml. of the diluted sample to a 250 ml. graduated flask containing 10 ml. of ammoniacal zinc chloride solution in about 20 ml. of water. Make up to mark, shake thoroughly and filter through a dry filter rejecting the first portion of the filtrate until clear. To a 50 ml. aliquot of the filtrate add one drop of methyl red solution and titrate to slight acidity with 10 per cent tartaric acid. Titrate using starch as indicator with 0.05 N iodine solution (y ml.).

1 ml. 0.05 N iodine = 0.0016 g. polysulphide sulphur

$$\text{Polysulphide sulphur} = \frac{8\,(x-y)}{w} \text{ per cent W/W}$$

$$= \frac{8\,(x-y) \times \text{apparent density}}{w} \text{ per cent W/V}$$

Note. The figure $(x - y)$ ml. should be less than 35 ml. (the amount of sodium sulphite solution added) thereby indicating that an excess of sodium sulphite has been used.

FORMALDEHYDE

SPECIFICATION

The specification refers to commercial formaldehyde sometimes called formalin.

1. *General*

The product shall consist essentially of an aqueous solution of formaldehyde with a suitable stabiliser. The product shall be a clear solution at ordinary temperatures but may on standing deposit a small amount of flocculent matter at low temperatures, e.g. 3° to 5° C.

2. *Content of Formaldehyde*

The product shall contain not less than 37.5 g. and not more than 40.5 g. formaldehyde (HCHO) per 100 ml. of product at 20° C. when tested by the prescribed method F 2.

3. *Acidity*

The product shall be neutral or faintly acid to litmus.

METHODS OF ANALYSIS

Sampling (F 1)

The general method of drawing samples shall be as follows :

Take a clean and dry glass tube of suitable bore (not less than 12 mm.) constricted at one end to an orifice 7 mm. in diameter and fitted at the other end with a rubber bung, through which passes a short piece of glass tubing connected to a convenient length of rubber tubing. Lower into the container in which the material is packed at a rate not exceeding 2 in. per second, the rubber tube remaining open. When the bottom of the container is reached constrict the rubber tube and carefully and slowly withdraw the tube full of liquid. Discharge the contents of the tube into the sample container.

When the consignment is packed in more than one container, sample a representative selection of packages in the manner prescribed. When the containers in the consignment are of more than one size, group together each size and sample and analyse the groups as separate consignments.

Select the number of containers for sampling from each consignment in accordance with the following scheme :

Number of equal-sized containers in the consignment	*Proportion of containers to be sampled*
Not exceeding 6	Every container
Exceeding 6 but not exceeding 40	6
„ 40 „ „ „ 70	8
„ 70 „ „ „ 100	10

When the number of equal-sized containers exceeds one hundred, divide them into the smallest possible number of groups of less than one hundred and sample each group separately, in accordance with the foregoing scheme.

Place the bulk sample in a clean, dry and air-tight glass-stoppered glass container of such size that it is nearly filled by the sample.

Determination of Formaldehyde Content F 2

REAGENTS

N sodium hydroxide solution
Hydrogen peroxide solution (10 vol. or 20 vol.)
N hydrochloric acid solution
Phenolphthalein solution (0.5 per cent in 50 per cent alcohol)

APPARATUS

2 250 ml. conical flasks
2 watch glasses
1 5 ml. graduated pipette
1 filter funnel

METHOD

Place 10 ml. of distilled water in a 250 ml. conical flask, cover with a watch glass and weigh accurately; add from a graduated pipette 3 ml. of the well-stirred formaldehyde solution, replace the watch glass and again weigh. Add 50 ml. of N sodium hydroxide solution, and immediately and slowly add through a funnel 50 ml. of hydrogen peroxide solution (10 vol.), or 25 ml. of hydrogen peroxide solution (20 vol.) and 25 ml. of water. At the same time mix 50 ml. of N sodium hydroxide solution with the same amount of hydrogen peroxide solution as used in the test, in a 250 ml. conical flask. Cover the flasks with watch glasses and allow them to stand with occasional shaking on a water bath at about 90° C. for 20 minutes. Cool to 20° C., add to each flask 0.2 ml. of phenolphthalein solution and titrate with N hydrochloric acid. (If necessary add more phenolphthalein solution towards the end, since the excess of hydrogen peroxide tends to "bleach" the colour.)

Let y = the difference between the two titres.

$$\frac{y \times 3}{\text{wt taken}} = \text{per cent formaldehyde W/W}$$

$$\frac{y \times 3 \times \text{density}}{\text{wt taken}} = \text{per cent formaldehyde, W/V (g. per 100 ml. at 20° C.)}$$

Note. If the original sample shows acidity to litmus, transfer 25 ml. to a 250 ml. conical flask, add 10 ml. of boiled and cooled distilled water and 0.2 ml. phenolphthalein solution and titrate with 0.1 N sodium hydroxide solution, and make the relevant correction in the above calculation.

Determination of Density of Formaldehyde Solution F 3

APPARATUS

A 50 ml. British Standard Density Bottle B.S. 733, 1937
A water bath at 20° C.

METHOD

Fill the tared bottle with distilled water at about 21° C. and place for 5 minutes in a water bath maintained at 20° C. Replace the stopper, wipe top and remove the bottle from the water bath, wipe adhering water from the sides of the bottle and weigh. Let W_W be the weight of water required to fill the bottle at 20° C.

Repeat this procedure using the formaldehyde in place of water.

Let W_F be the weight of formaldehyde required to fill the bottle at 20° C.

$$\text{The density at 20° C. (g. per ml.)} = \frac{W_F \times 0.9982}{W_W}$$

Note. The identity of the aldehyde present may be confirmed by the dimedone test (*Industrial and Engineering Chemistry* (Anal. Ed). 1931, **3**, 365).

METALDEHYDE

SPECIFICATION

The specification refers to metaldehyde in the form of a fine white powder or tablets which readily crush to a fine white powder.

Content of Metaldehyde

The product shall contain not less than 95 per cent by weight of metaldehyde expressed as CH_3CHO when analysed by the method prescribed, M 2.

METHODS OF ANALYSIS

Sampling (M 1)

A representative sample of the material, taken from the bulk, is necessary for the purpose of examination under this specification. The sample shall be packed in a suitable clean and dry metal or glass container.

Determination of Metaldehyde Content M 2

REAGENTS

0.5 N hydrochloric acid

N sodium hydroxide solution

Hydroxylamine hydrochloride solution 10 per cent. Dissolve 10 g. of hydroxylamine hydrochloride (A.R.) in 100 ml. of distilled water and neutralize to bromophenol blue by adding N sodium hydroxide solution drop by drop

Bromophenol blue solution (0.04 per cent). Dissolve 0.4 g. of bromophenol blue and 6 ml. of 0.1 N sodium hydroxide solution in a litre of 20 per cent alcohol

APPARATUS

1 250 ml. round-bottomed flask

1 air condenser

1 water bath

METHOD

Weigh out accurately from 0.9 to 1.1 g. of the well-mixed sample (after powdering in the case of tablets) into a 250 ml. round-bottomed flask fitted with a ground-in air condenser. Add 30 ml. of neutral hydroxylamine solution followed by 20.0 ml. of 0.5 N hydrochloric acid and 100 ml. of water. Place the air-condenser in position and heat the flask and its contents on a boiling water bath with occasional shaking, until all the metaldehyde has dissolved and then heat for a further thirty minutes. Cool the flask and its contents, rinse down the condenser tube with 10 to 15 ml. of distilled water, remove the condenser and titrate with N sodium hydroxide solution until a blue colour is obtained which matches that of 30 ml. of neutral hydroxylamine solution diluted to 100 ml. with distilled water.

Carry out a blank determination on 20.0 ml. of 0.5 N hydrochloric acid using bromophenol blue as indicator.

Let ml. N NaOH required in test = A
Let ml. N NaOH required in blank = B

$$\frac{(A-B) \times 4.405}{\text{wt taken}} = \text{metaldehyde calculated as per cent acetaldehyde}$$

Mix 5 g. of the powdered sample with 10 ml. of alcohol (industrial methylated spirits 64° O.P.), if necessary previously neutralized, add 50 ml. of water and bromophenol blue solution and titrate with N sodium hydroxide solution. Make the relevant correction for acidity (if any) in the above calculation.

NICOTINE

SPECIFICATION

Content of Nicotine

Nicotine shall be defined as the mixed alkaloids of tobacco. It shall contain not less than 95 per cent weight in weight of nicotine as determined by the prescribed method, N 1.

NICOTINE SULPHATE

SPECIFICATION

1. *Content of Nicotine*

Nicotine sulphate shall be defined as the sulphates of the mixed alkaloids of tobacco. It shall contain not less than 40 per cent weight in weight of nicotine as determined by the prescribed method, N 1.

2. It shall not yield a sediment when mixed with five times its own volume of water.

METHOD OF ANALYSIS

Sampling

The sample should be well mixed before a portion is taken for analysis.

Determination of Nicotine Content N 1

REAGENTS

Acetic acid solution (15 per cent W/V)
Sodium hydroxide solution (10 per cent W/V)
Hydrochloric acid solution (2N)
Hydrochloric acid solution (1 in 1,000)
Methyl red indicator solution
Silico-tungstic acid solution (12 per cent W/V). This solution should be prepared from the salt of formula $4H_2O.SiO_2.12WO_3.22H_2O$ and must give with nicotine a crystalline precipitate which readily settles and is easily filterable

APPARATUS

1 stoppered weighing bottle or other suitable closed vessel
1 steam distillation apparatus (preferably with glass joints) fitted with dropping funnel, anti-splash head, condenser and adapter
1 250 ml. beaker
1 750 ml. beaker
1 litre graduated flask
1 50 ml. pipette
1 10 ml. pipette
2 25 ml. graduated cylinders
1 100 ml. graduated cylinder
1 asbestos-packed Gooch or other suitable filter

METHOD

Precautions must be taken at all stages to prevent loss of nicotine. Weigh by difference in the stoppered weighing bottle or other suitable closed vessel a quantity of the sample containing 1-2 g. of nicotine. Transfer to the distillation flask with about 100 ml. of water, add a little pumice if necessary to prevent bumping, and connect the distillation apparatus. Add by means

of the dropping funnel 10 ml. of the sodium hydroxide solution. Steam distil, with the adapter dipping into 10 ml. of hydrochloric acid (2N) containing methyl red indicator, until the distillate is free from nicotine, i.e. until a few ml. show no opalescence when treated with a drop of the silico-tungstic acid solution and a drop of hydrochloric acid (2N). Transfer the distillate to a 1 litre graduated flask, make up to the volume with water and mix.

To 50 ml. of the solution add 10 ml. of hydrochloric acid (2N) and an excess of silico-tungstic acid solution. Between 10 and 15 ml. may be required. Stir until the precipitate crystallizes and allow to stand for 4 hours. Filter and wash the precipitate with dilute hydrochloric acid (1 in 1000) until the washings are free from silico-tungstic acid, and then with a little distilled water. Dry and ignite the precipitate.

Residue $\times$ 0.114 = nicotine

Note 1. To reduce possible error due to absorption of moisture while weighing, if the sample permits weigh a quantity containing 10–20 g. of nicotine, transfer to a 500 ml. graduated flask with water, make up to the 500 ml. volume, mix, and take 50 ml. of this solution for analysis.

Note 2. When the presence of pyridine is known or suspected, transfer the weighed quantity of the sample to the distillation flask with 100 ml. of the acetic acid solution, add a little pumice if necessary, and steam distil until approximately 250 ml. of distillate are obtained. Reject the distillate.

Without disconnecting the apparatus, allow the distillation flask to cool and add 35 ml. of the sodium hydroxide solution. Steam distil and continue the analysis on the distillate as described.

Note 3. When the distillation of nicotine is well under way, heat the distillation flask to reduce the volume of liquid as far as practicable without bumping or undue separation of insoluble matter.

Note 4. The precipitate should be ignited gently until all carbon is oxidised and then for no longer than 10 minutes over the full heat of a Meker burner.

LEAD ARSENATE

LEAD ARSENATE POWDER

SPECIFICATION

The lead arsenate referred to in this specification shall be essentially di-plumbic arsenate ($PbHAsO_4$).

Lead arsenate powder shall be a fine powder free from lumps and grit.

1. *Content of Lead*

The material shall contain not less than 62 per cent lead oxide (PbO) when determined by the prescribed method LA 2.

2. *Content of Arsenic*

The material shall contain not less than 32 per cent of arsenic calculated as arsenic pentoxide (As_2O_5) when determined by the prescribed method LA 3.

3. *Content of water-soluble Arsenic*

The material shall contain not more than 0.25 per cent of arsenic calculated as arsenic pentoxide (As_2O_5) soluble in water when determined by the prescribed method LA 4.

4. *Acidity*

The material shall show no alkalinity and the acidity shall not exceed 0.2 per cent calculated as nitric acid when determined by the prescribed method LA 5.

5. *Size of Particles*

The material shall pass completely through an 80 mesh sieve (B.S. 410, 1943) and not more than 5 per cent shall be retained on a 300 mesh sieve (B.S. 410, 1943) when tested by the prescribed method LA 6.

Note. Some manufacturers offer powder lead arsenate containing spreaders or wetting agents. In such cases the limits given under (1) and (2) may not apply and in these circumstances the manufacturer shall declare the content of lead arsenate conforming to the above specification. This shall be not less than 97 per cent.

LEAD ARSENATE PASTE

SPECIFICATION

The lead arsenate referred to in this specification shall be essentially di-plumbic arsenate ($PbHAsO_4$).

Lead arsenate paste shall consist essentially of a mixture of di-plumbic arsenate ($PbHAsO_4$) and water. Lead arsenate paste shall be of a uniform consistency, free from lumps and hard particles, and shall readily rub down to a fine cream with water.

1. *Content of Lead*

The material shall contain not less than 28.4 per cent of lead oxide (PbO) when determined by the prescribed method LA 2.

2. *Content of Arsenic*

The material shall contain not less than 14 per cent of arsenic calculated as arsenic pentoxide (As_2O_5) when determined by the prescribed method LA 3.

3. *Content of Water*

The material shall contain not more than 52 per cent of water when determined by the prescribed method LA 1.

4. *Content of water-soluble Arsenic*

The material shall contain not more than 0.25 per cent of arsenic calculated as arsenic pentoxide (As_2O_5) soluble in water calculated on the dry basis when determined by the prescribed method LA 4.

5. *Acidity*

The material shall show no alkalinity and the acidity calculated on the dry basis shall not exceed 0.2 per cent calculated as nitric acid when determined by the prescribed method LA 5.

The manufacturer shall declare the percentage of arsenic expressed as arsenic pentoxide (As_2O_5) in the paste. Pastes are normally sold with a content of either 15 per cent or 20 per cent of arsenic pentoxide (As_2O_5).

METHODS OF ANALYSIS

Sampling

The greatest care must be exercised in taking samples for any purpose. They must be truly representative of the bulk of the material.

Determination of Moisture Content LA 1

APPARATUS

1 oven at 105°-110° C.

METHOD

Dry 10 g. lead arsenate paste at 105°-110° C. to constant weight and express the loss as a percentage of the original weight.

Determination of Lead Content LA 2

REAGENTS

Dilute nitric acid (1:3)
Concentrated sulphuric acid
Alcohol 95 per cent or industrial methylated spirits

APPARATUS

1 digestion flask
1 filter
1 250 ml. beaker
1 sintered glass crucible porosity G 4

METHOD

Digest 0.5 g. lead arsenate powder or 1 g. lead arsenate paste with 25 ml. dilute nitric acid (1 vol. concentrated acid to 3 vols. distilled water) until solution is apparently complete. Filter off any insoluble matter and wash the filter with distilled water until free from acid. Add 5 ml. concentrated sulphuric acid to the filtrate and evaporate on a sand bath until white fumes are evolved. Cool, dilute with 10 ml. distilled water, and again evaporate until white fumes are evolved. Cool, dilute with 50 ml. of a mixture of equal parts 95 per cent alcohol (or industrial methylated spirits) and distilled water, allow to stand for 30 minutes, filter on a sintered glass filter (porosity G4) and wash with 95 per cent alcohol (or industrial methylated spirits) until free from acid. Dry the precipitate of lead sulphate to constant weight.

1 g. lead sulphate ($PbSO_4$) = 0.7360 g. lead oxide (PbO)

Determination of Total Arsenic* LA 3

REAGENTS

Concentrated sulphuric acid
0.1 N iodine
Red phosphorus (passing 100 mesh)
5N sodium hydroxide
Sodium bicarbonate
Starch solution

APPARATUS

1 250 ml. beaker
1 Gooch crucible with asbestos pad
1 burette
1 filter flask

METHOD

Weigh accurately and transfer to a beaker approximately 0.5 g. lead arsenate powder or 1.0 g. lead arsenate paste (representing about 0.15 g. As_2O_5). Add 20 ml. distilled water and 5 ml. concentrated sulphuric acid (sp. gr. 1.84) followed by 2 ml. 0.1N iodine solution and 0.2 g. red phosphorus sufficiently fine to pass through a 100 mesh sieve.

Heat the contents of the beaker to boiling point and maintain at this temperature until reduction is complete (approximately 3 mins.), i.e. until the yellow colour (due to free iodine) has disappeared and the solution is colourless with the exception of particles of red phosphorus in suspension. Filter the warm mixture through a Gooch crucible with asbestos pad and wash the residue with three successive portions of 10 ml. distilled water. Nearly neutralise the filtrate with 5N sodium hydroxide solution, add an excess of sodium bicarbonate to the slightly acid solution and titrate with 0.1 N iodine solution.

1 ml. 0.1 N iodine = 0.00575 g. arsenic pentoxide (As_2O_5)

* This method is based on that of FitzGibbon (*Analyst*, 1933, **38**, 469).

Determination of Water-Soluble Arsenic LA 4

REAGENTS

0.01 N iodine

The following may also be required:

Concentrated nitric acid
Fuming nitric acid (sp. gr. 1.5)
Sodium bicarbonate
Dilute sulphuric acid (1 : 10)
Sulphur dioxide

APPARATUS

1 stoppered vessel 500 ml. capacity
1 mechanical shaker (at 30° C.)
1 filter funnel and dry filter paper

METHOD

Weigh accurately 2.5 g. lead arsenate powder or 5 g. lead arsenate paste and mix with 250 ml. recently boiled and cooled distilled water in a stoppered vessel of about 500 ml. capacity. Place in a warm place (i.e., at a temperature of about 30° C.) and shake mechanically for 2 hours. Cool and filter through a dry filter paper. The filtrate must be clear and it may be necessary to centrifuge. Reduce the arsenic in 50 ml. of the filtrate and proceed as described in LA 3, but titrate with 0.01 N solution of iodine using starch as indicator. (See note.)

1 ml. 0.01 N iodine = 0.000575 g. arsenic pentoxide (As_2O_5)

Note. If the value for water-soluble arsenic is higher than 0.2 per cent, it is advisable to carry out a check determination by total oxidation. The procedure is as follows:

To 50 ml. of the filtrate obtained as described in LA 4 above, add 5 ml. concentrated nitric acid and evaporate to dryness on a water bath. Add a further 5 ml. fuming nitric acid (sp. gr. 1. 5) and again evaporate to dryness. Dilute to 50 ml. with distilled water, add 1 ml. dilute sulphuric acid (1 part concentrated sulphuric acid to 10 parts water) and saturate the solution with sulphur dioxide. Boil off the excess sulphur dioxide (a few fine particles of porous pot prevent bumping). Cool, add excess sodium bicarbonate and titrate with 0.01 N iodine using starch as indicator.

Determination of Acidity LA 5

REAGENTS

0.01 N sodium hydroxide solution
Phenolphthalein indicator solution

APPARATUS

1 1,000 ml. graduated flask
1 filter funnel and paper
1 100 ml. measuring cylinder
1 burette

METHOD

Mix 25 g. lead arsenate powder or a quantity of paste containing 25 g. lead arsenate and make up to 1,000 ml. with recently boiled and cooled distilled water and shake thoroughly for 15 minutes. Filter and titrate 100 ml. of the filtrate with 0.01 N sodium hydroxide using phenolphthalein as indicator.

1 ml. 0.01 N sodium hydroxide = 0.00063 g. nitric acid

Determination of Particle Size LA 6

APPARATUS

1 500 ml. beaker flask
1 250 ml. measuring cylinder
1 80 mesh sieve B.S. 410, 1943
1 300 mesh sieve B.S. 410, 1943
1 soft camel hairbrush
1 tared vessel
1 oven at 98°-102° C.

METHOD

Add 250 ml. distilled water at 60°C. to 20 g. lead arsenate powder in a 500 ml. beaker flask and mix by gently swirling, and allow to stand for one hour. Wash the whole through the 80 mesh sieve, gently brush the residue with a soft camel hair brush and wash with water until the washings passing through the sieve are clear. Transfer the residue to a tared vessel, dry and weigh.

Repeat this procedure using the 300 mesh sieve.

PARIS GREEN

SPECIFICATION

This specification is intended to apply to Paris Green used solely for the control of plant pests.

Paris Green (Emerald Green, Schweinfurth Green) shall be a copper aceto-arsenite and shall be a fine green powder, free from added colouring matter.

1. *Copper Content*

The material shall contain not less than 30 per cent by weight of copper expressed as CuO when determined by the prescribed method PG 2.

2. *Arsenic Content*

The material shall contain not less than 55 per cent by weight of arsenic expressed as arsenious oxide (As_2O_3) when determined by the prescribed method PG 2.

3. *Content of Water-Soluble Arsenic*

The material shall contain not more than 1.5 per cent arsenic expressed as As_2O_3 soluble in water when determined by the prescribed method PG 4.

4. *Acetate Content*

The material shall contain not less than 10 per cent of acetate expressed as acetic acid when determined by the prescribed method PG 3.

5. *Size of Particles*

The material shall pass completely through an 80 mesh B.S. sieve and not more than 5 per cent shall be retained on a 300 mesh B.S. sieve when tested by the prescribed method PG 5.

METHODS OF ANALYSIS

Sampling PG 1

The method to be used will depend upon circumstances, but is to be based upon B.S. 1016, 1942.

Determination of Arsenic and Copper Content* PG 2

REAGENTS

Crystalline oxalic acid (A. R.)
Sodium bicarbonate (A. R.)
Dilute sulphuric acid (1 : 10)
Starch solution
Potassium permanganate solution (0.1N)
Aqueous iodine solution (0.1N)

* This method is based on the method of Peters and Fielding (*Jour. Ind. Eng. Chem.*, 1916, **8**, 1114).

APPARATUS

1 150 ml. beaker
1 filter (asbestos or sintered glass)
2 burettes
1 50 ml. measuring cylinder

METHOD

Weigh accurately about 0.25 g. Paris Green and place in a 150 ml. beaker, add less than 1 ml. of dilute sulphuric acid, dilute with water to 50 ml. and boil for two minutes. While still hot, add cautiously and slowly 2 g. crystalline oxalic acid and again heat to boiling (see Note 1). Allow to stand until cool.

Filter off the precipitated copper oxalate on an asbestos or sintered glass filter, and wash the precipitate with a little water to carry all the arsenic into the filtrate. Reserve the filtrate for the determination of arsenic content. Return the filter and its contents to the original beaker, add a convenient quantity (50 ml.) of water and 5-10 ml. of dilute sulphuric acid. Heat nearly to boiling and titrate the liberated oxalic acid with standard potassium permanganate solution (Note 2).

1 ml. of 0.1 N potassium permanganate solution = 0.003979 g. CuO

The filtrate remaining from the precipitation of the copper contains oxalic and sulphuric acids, which are neutralized by the addition of solid sodium bicarbonate; add a further 1-2 g. solid sodium bicarbonate and titrate the solution with the 0.1N aqueous solution of iodine until a permanent blue colour is obtained after 1 ml. of 1 per cent starch solution has been added.

1 ml. of 0.1 N aqueous iodine solution = 0.004948 g. As_2O_3

Note 1. In adding crystalline oxalic acid to the hot solution, it is advisable to add the first few crystals slowly, otherwise the solution will tend to superheat and will boil if the whole quantity of oxalic acid is added at one time.

Note 2. The end point in this titration is slow, and depends upon the speed with which oxalic acid is liberated, the latter being governed by the concentration of sulphuric acid and the temperature of the system. The end point, however, is sharp and must not be overstepped.

Determination of the Acetate Content PG 3

REAGENTS

Concentrated sulphuric acid
0.5 N potassium hydroxide solution
Phenolphthalein indicator solution

APPARATUS

1 200 ml. distillation flask
1 splash head
1 water-cooled Liebig condenser
1 steam generator

METHOD

Weigh accurately about 5 g. Paris Green and place in a 200 ml. distillation flask with 40 ml. distilled water and 10 ml. concentrated sulphuric acid.

Connect the flask with a steam generator and steam distil until approximately 200 ml. of liquid have been collected, heating the distillation flask so that the volume of the contents (50 ml.) remains approximately constant.

Titrate the distillate with 0.5 N potassium hydroxide solution using phenolphthalein as indicator.

1 ml. 0.5 N potassium hydroxide solution = 0.03 g. acetic acid

Determination of Water-Soluble Arsenic PG 4

REAGENTS

Sodium bicarbonate (A.R.)
0.01 N aqueous iodine solution
Starch solution

APPARATUS

A mechanical agitator
1 vacuum flask (1 pint capacity)
1 filter funnel and paper
1 100 ml. measuring cylinder
1 burette

METHOD

Weigh accurately about 0.5 g. Paris Green and place in the flask together with 250 ml. freshly-boiled distilled water at 20° C. Stopper the flask securely and shake mechanically for 2 hours.

Remove the flask and filter the solution.

To 100 ml. aliquot of this solution, add 1 g. sodium bicarbonate and 1 ml. of 1 per cent starch indicator solution and titrate with 0.01N aqueous iodine solution until a permanent blue colour is obtained.

1 ml. 0.01 N iodine solution = 0.0004948 g. As_2O_3

Determination of Particle Size PG 5

REAGENT

White spirit (B.S. 245, 1936)

APPARATUS

1 100 ml. measuring cylinder
1 80 mesh sieve B.S. 410, 1943
1 300 mesh sieve B.S. 410, 1943
1 soft camel hair brush
1 tared vessel
1 oven at 98°-102°C.

METHOD

Mix 10 g. of the Paris Green with 100 ml. standard white spirit (B.S. No. 245) and wash as much as possible of the mixture through a 300 mesh B.S. sieve with more white spirit. Gently brush the residue remaining on the sieve with a soft camel hair brush. Again wash with spirit until the washings are clear. Wash the final residue from the sieve with spirit into a suitable tared vessel, decant excess spirit, and dry at 98°-102° C. to constant weight.

Repeat the operation using an 80 mesh B.S. sieve.

The material shall be considered to comply with the specification if no residue remains on an 80 mesh B.S. sieve and not more than 5 per cent on a 300 mesh B.S. sieve.

TAR OIL WASHES

MISCIBLE TAR OIL WINTER WASHES

SPECIFICATION

The following specification refers only to single phase products compounded from distillates from horizontal or vertical retort tars or coke oven tars.

1*. *Content of Total Oil*

The wash shall yield not less than 80 per cent by weight of total oil when analysed by the prescribed method T 4.

* See footnote on page 21.

2*. *Content of Tar Oil Soluble in Dimethyl Sulphate*

Not less than 52 per cent by weight of the wash shall be tar oil soluble in dimethyl sulphate, when determined by the prescribed method T 6.

3. *Content of Phenols*

Not more than 10 per cent by weight of the wash shall be phenols, when determined by the prescribed method T 3.

4. *Distillation Range*

The neutral oil soluble in dimethyl sulphate shall have a distillation range, when determined by the prescribed method T 7, such that:

the fraction distilling above 230° C. shall constitute at least 40 per cent by weight of the wash,

the fraction distilling above 290° C. shall constitute at least 22 per cent by weight of the wash,

the fraction distilling above 335° C. shall constitute at least 10 per cent by weight of the wash.

5. *Stability*

(*a*) The undiluted wash shall conform to the prescribed test for stability T 8 (a).

(*b*) The diluted wash shall conform to the prescribed test for stability T 9.

STOCK EMULSION TAR OIL WINTER WASHES SPECIFICATION

The following specification refers only to polyphase products compounded from distillates from horizontal or vertical retort tars or coke oven tars.

1. *Content of Neutral Oil*

The wash shall yield not less than 60 per cent by weight of neutral oil, when analysed by the prescribed method T 1.

2. *Content of Neutral Oil Soluble in Dimethyl Sulphate*

Not less than 54 per cent by weight of the wash shall be neutral oil soluble in dimethyl sulphate, when determined by the prescribed method T 5.

3. *Content of Phenols*

Not more than 5 per cent by weight of the wash shall be phenols, when determined by the prescribed method T 3.

4. *Distillation Range*

The neutral oil soluble in dimethyl sulphate shall have a distillation range, when determined by the prescribed method T 7, such that:

the fraction distilling above 230° C. shall constitute at least 48 per cent by weight of the wash,

the fraction distilling above 290° C. shall constitute at least 27 per cent by weight of the wash,

the fraction distilling above 335° C. shall constitute at least 11 per cent by weight of the wash.

* The items specified in Sections 1 and 2 differ from those in the corresponding sections of the Stock Emulsion Specification. This difference has been made, not on any technical grounds, but because the Miscible Oil Specification was provisionally made available to manufacturers and growers some time ago and has become familiar in its present form.

5. *Stability*

(*a*) The undiluted wash shall conform to the prescribed test for stability T 8 (b).

(b) The diluted wash shall conform to the prescribed test for stability T 9.

METHODS OF ANALYSIS*

Sampling

The method of sampling will depend upon the circumstances and is to be based on B.S. 616, 1938, *Sampling of Coal Tar and its Products*, or *Standard Methods for Testing Tar and its Products*, 2nd Ed., 1938, page 13 *et seq.* The manufacturer's instructions, if any, for diluting the product should accompany the sample, which should not be less than one quart in volume.

Determination of Neutral Oil Content T 1

REAGENTS

- Sodium hydroxide solution (10 per cent W/W)
- Sodium hydroxide solution (1 per cent W/W)
- Hydrochloric acid solution (4 per cent W/W)
- Ether (see Appendix D, p. 62)
- Sodium chloride solution (saturated)
- Anhydrous sodium sulphate

APPARATUS

- 2 separating funnels (1500 ml. capacity)
- 1 filter funnel
- 1 Buchner funnel with filter flask
- 1 Liebig condenser (not less than 30″ water jacket) and adapter
- 1 desiccator
- 1 200 ml. extraction flask
- 1 1000 ml. lipped beaker
- 1 2000 ml. conical flask
- 1 1500 ml. conical flask
- 1 wash bottle of dry ether
- 1 splash head, with side inlet
- 1 water or steam bath
- 1 hot water or steam oven at 98° C. ± 2°

METHOD

Weigh accurately about 50 ml. of the well-shaken sample. Wash into the 1500 ml. separating funnel with 500 ml. water. Add 100 ml. of 10 per cent sodium hydroxide solution and 500 ml. of ether. Shake and allow to stand until a clear ether layer has separated. If the emulsion has not broken sufficiently after standing overnight, add 10 ml., or more if necessary, of saturated sodium chloride solution and rotate gently until the emulsion breaks (see Note).

Note. Stock Emulsion Tar Oil Winter Washes. Certain emulsions are not completely broken after a short period when treated in this manner. A partial separation of either the ether or the aqueous layer is obtained. By withdrawing the clear phase and replacing with water or ether, according to the phase removed, a complete separation is eventually obtained.

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* The possibilities that high-boiling hydrocarbons soluble in dimethyl sulphate may be produced from sources other than tar, or that methods may be devised for the recovery from tar oils of fractions of abnormal ovicidal properties, are not covered by the analytical methods. These possibilities are hypothetical and do not constitute a practical defect of the present specifications, but it should be noted that the specifications and methods of analysis refer only to washes compounded from distillates from horizontal or vertical retort tar or from coke oven tar. This proviso does not exclude the addition of petroleum oils.

Further, the analytical procedure prescribed for the determination of the amounts of neutral oil soluble in dimethyl sulphate recovered over the specified distillation ranges will give results not necessarily exactly coinciding with the amounts calculated on the basis of the percentage and distillation range of the neutral tar oil originally incorporated in the wash. The amounts recovered are influenced by the distillation range of the neutral oil soluble in dimethyl sulphate, relative to the distillation range of that insoluble in dimethyl sulphate, which might be present in the compounded products. The divergence is noteworthy only when these ranges differ widely.

Withdraw the lower layer into the second 1500 ml. separating funnel and to this add 200 ml. of ether and shake. After allowing to stand for one hour, withdraw the lower layer into the lipped beaker and add the ether layer to that from the first extraction which remains in the first separating funnel.

Return the alkaline layer to the empty separating funnel and repeat its extraction with 200 ml. lots of ether until the ether layer is lighter in colour than 0.001 N aqueous iodine solution. (In all, 3 or 4 washings with 200 ml. lots of ether are usually sufficient.) Add the ether washings to the first separating funnel and wash with successive 50 ml. lots of 1 per cent sodium hydroxide solution until the aqueous layer is almost colourless. (3 or 4 washings are usually required.) Wash once with 100 ml. of distilled water. Combine and reserve the aqueous layer and washings in the beaker.

Extract the combined ether layers with successive 100 ml. lots of 4 per cent hydrochloric acid until the acid layer is lighter in colour than 0.001 N aqueous iodine solution. (If, as usually occurs, much carbonaceous matter is precipitated by the acid treatment, it may be convenient to filter by means of a filter pump at this stage and to wash the sludge with ether and reject the residue.)

Unite the acid layers, transfer to the second separating funnel and wash twice with 50 ml. lots of ether. (The carbonaceous sludge, if not already removed, is usually held by the ether layer. To secure a good separation it may be convenient to add small amounts (20 ml.) of distilled water after the bulk of the acid layer has been withdrawn.)

Reserve the acid layer for the recovery of tar bases.

Add the ether washings to the main bulk of the ether extract in the first separating funnel and wash once with 100 ml. water. Reject the aqueous washing. Transfer the ether solution to the large conical flask and concentrate to 250-300 ml. on the water bath, distilling the ether through the water-cooled Liebig condenser. When cool, transfer to a dry flask, shake well with 20 g. anhydrous sodium sulphate and allow to stand overnight.

Filter the ether solution through an open-textured filter paper, collecting the first 100 ml. of the filtrate in the tared extraction flask and the remainder in another flask. Transfer the residual sodium sulphate from the conical flask to the filter paper by means of successive 50 ml. lots of ether (previously dried over anhydrous sodium sulphate) and finally wash the residue and filter paper with dry ether from a wash bottle until the filtrate is lighter in colour than 0.001 N aqueous iodine solution, collecting the washings in the second flask.

Distil the ether from the first 100 ml. of the filtrate on the water or steam bath, using the water-cooled Liebig condenser to which the extraction flask is attached via the splash head. Add the combined washings and remainder of the filtrate to the residue in the extraction flask at suitable stages, or, if convenient, by means of a suitable separating funnel, the delivery tube of which is inserted through the cork of the extraction flask.

Remove the last traces of ether by transferring the flask to the oven at 98° C. $\pm$ 2° for 30 minutes, displacing the ether vapour present in the flask by a puff of air from the bellows at 10 minute intervals.

Transfer the flask to the desiccator and, when cool, reweigh and calculate the percentage (W/W) of neutral oil in the wash. The method may be expected to give an accuracy of $\pm$ 2. This should be borne in mind when interpreting the results.

Determination of Tar Bases Content T 2

Miscible Tar Oil Winter Washes

REAGENTS

Sodium hydroxide solution (10 per cent W/W)
Ether (see Appendix D, p. 62)
Anhydrous sodium sulphate

APPARATUS

2 separating funnels (1000 ml. capacity)
1 Liebig condenser (not less than 30″ water jacket) and adapter
1 desiccator
1 200 ml. extraction flask
1 splash head, with side inlet
1 water or steam bath
1 hot water or steam oven at 98° C. ± 2°

METHOD

Transfer the acid washings from the neutral oil determination to a 1000 ml. separating funnel. Make alkaline to litmus paper with 10 per cent sodium hydroxide solution, keeping cool under the tap. Add 100 ml. of ether, shake and allow to stand for one hour. Withdraw the alkaline layer into the second separating funnel and extract again with 100 ml. of ether.

Repeat this operation until the ether extract is only faintly coloured.

Unite the ether washings. Transfer to a dry flask, shake well with 10 g. anhydrous sodium sulphate and allow to stand overnight.

Recover the tar bases by removing the ether as described under Determination of Neutral Oil Content T 1.*

Transfer the flask to the desiccator and, when cool, reweigh and calculate the percentage (W/W) of tar bases in the wash.

Determination of Phenols Content T 3

REAGENTS

Barium hydroxide (A.R.)
Hydrochloric acid (A.R. 32 per cent W/W)
Anhydrous sodium sulphate
Barium chloride solution (10 per cent W/V)
Ether (see Appendix D, p. 62)
Methyl orange solution

APPARATUS

1 2000 ml. conical flask
1 Buchner funnel with 2000 ml. filter flask
1 200 ml. extraction flask
1 Liebig condenser (not less than 30″ water jacket) and adapter
1 hot-water or steam oven at 98° C. ± 2°
2 1500 ml. separating funnels
1 beaker (not less than 2000 ml. capacity)
1 splash head, with side inlet
1 water or steam bath
1 desiccator

METHOD

Transfer the alkaline layers and washings from the neutral oil determination to the large conical flask and remove dissolved ether by distillation until the solution begins to form a persistent froth. Cool somewhat, and pour carefully into the large beaker containing 10 g. solid barium hydroxide. Place on the boiling water bath and stir until the precipitate has coagulated. Test

* There may be some loss, up to 5 per cent of the bases, but this is not considered important.

for complete precipitation of soaps by the non-formation of precipitate on the addition of a few drops of barium chloride solution. Filter hot through the Buchner funnel with suction and wash the precipitate with three successive 50 ml. lots of hot water.

Add 1-2 ml. 0.1 per cent methyl orange solution to the filtrate and acidify with concentrated hydrochloric acid. When cold, transfer to the separating funnel, shake with 100 ml. ether and allow to stand one hour. Withdraw the aqueous layer to the second separating funnel and extract with successive 100 ml. lots of ether (3 or 4 extractions are usually sufficient) until the ether extract is lighter in colour than 0.001 N aqueous iodine solution.

Unite the ether washings and the ether extract in the first separating funnel and wash once with 100 ml. distilled water. Transfer to a dry flask, shake well with 10 g. anhydrous sodium sulphate and allow to stand overnight.

Recover the phenols by removing the ether as described under Determination of Neutral Oil Content T 1.

Transfer the flask to the desiccator and, when cool, reweigh and calculate the percentage (W/W) of phenols in the wash.

The method may be expected to give an accuracy of $\pm$ 1. This should be borne in mind when interpreting the results.

Determination of Total Oil Content T 4

Miscible Tar Oil Winter Washes

The content of total oil in the miscible washes is calculated by adding together the percentages of neutral oil, phenols and tar bases as determined above.

Determination of Neutral Oil Soluble in Dimethyl Sulphate T 5

REAGENT

Dimethyl sulphate. See Appendix A, page 61. (To ensure freedom from acid, the dimethyl sulphate should be shaken the day before use with excess of anhydrous sodium carbonate, from which it is filtered immediately before it is required.)

APPARATUS

A pear-shaped, glass-stoppered separating funnel of 150 ml. capacity with delivery tube cut as short as possible and ground at right-angles to the axis. Alternatively, the delivery jet may have a capillary bore equal in diameter to that of the tap. A wire is attached to the funnel, in such a manner that the funnel can be weighed on an ordinary analytical balance.

Manipulation is greatly facilitated if the funnel is graduated from the closed tap from 0-150 ml.

METHOD

Pour into the weighed separating funnel a known volume of about 30 ml. of the neutral oil and reweigh the funnel and oil. Add to the oil twice its volume of dimethyl sulphate, shake thoroughly, release the stopper and allow the funnel to stand upright overnight at room temperature.

Withdraw the lower layer slowly until the interface is at the bottom of the tap bore. Remove traces of the dimethyl sulphate layer from the delivery tube by means of a roll of filter paper. If the bore of the delivery tube is of the same diameter as that of the tap, the interface can be run to the bottom of the tube, the final drop of dimethyl sulphate being removed with filter paper. Reweigh the funnel and the neutral oil insoluble in dimethyl sulphate.

Calculate the percentage of neutral oil soluble in dimethyl sulphate on the basis of neutral oil and thence as a percentage of the wash.

The method may be expected to give an accuracy of ± 2 in the figure for dimethyl sulphate soluble neutral oil as percentage (W/W) of the wash. This should be borne in mind when interpreting the results.

Determination of Content of Tar Oil Soluble in Dimethyl Sulphate T 6

Miscible Tar Oil Winter Washes

In the case of the miscible washes, the content of tar oil soluble in dimethyl sulphate is obtained by adding to the figure for the content of neutral oil soluble in dimethyl sulphate obtained above, the percentages of phenols and tar bases.

The method may be expected to give the content of tar oils soluble in dimethyl sulphate expressed as a percentage (W/W) of the wash with an accuracy of ± 2.

Determination of Distillation Range of Neutral Tar Oil T 7

(*i*) Recovery of Neutral Oil

Reagents

Sodium hydroxide solution (50 per cent W/W)
Anhydrous sodium sulphate
Ether (see Appendix D, p. 62)
Hydrochloric acid (4 per cent W/W)
Sodium chloride solution (saturated)

Apparatus

2 separating funnels (not less than 2000 ml. capacity)
1 Liebig condenser (not less than 30″ water jacket) and adapter
1 wide 100 ml. beaker
1 1000 ml. conical flask
1 separating funnel (1500 ml. capacity)
1 splash head with side inlet
1 water or steam bath
1 thermometer (0-200°C.)
1 250 ml. distillation flask
1 air condenser (Type 3 B.S.658, 1936)

Method

(a) *Miscible Tar Oil Winter Washes*

Transfer to the first large separating funnel approximately 200 ml. of the sample, 1000 ml. distilled water, 50 ml. of the sodium hydroxide solution and 500 ml. ether. Shake and allow to stand overnight.

Withdraw the alkaline layer into the second separating funnel, and, if an intermediate layer of salted-out soap has formed, transfer this to the 1500 ml. separating funnel.

Extract the alkaline layer with three successive 100 ml. lots of ether. To the intermediate layer (if present) add 500 ml. distilled water and extract with three successive 100 ml. lots of ether.

(b) *Stock Emulsion Tar Oil Winter Washes*

Transfer to the first large separating funnel, approximately 200 ml. of the sample, 1000 ml. distilled water and 500 ml. ether. Add at least 10 ml. of the sodium hydroxide solution and, if necessary, saturated salt solution in amounts found by previous experience (under Determination of Neutral Oil Content T 1) to be required to break the emulsion.

When a satisfactory separation of aqueous and ether layers has been obtained, transfer the aqueous layer to the second separating funnel and extract with three successive 200 ml. lots of ether.

With washes of both types, continue the method as follows:

Unite all the ether extracts in the first separating funnel and wash once with 200 ml. distilled water. Reject this wash water and all ether-extracted alkaline layers.

Wash the combined ether extracts with successive 100 ml. lots of 4 per cent hydrochloric acid until the acid washings are lighter in colour than 0.001 N aqueous iodine solution. Carbonaceous sludge, if troublesome, may be filtered off at the pump. Reject all acid washings. Concentrate the ether solution to 400-600 ml. on the water bath, distilling the ether through the water-cooled Liebig condenser. Cool the concentrated ether solution, transfer to a dry flask and shake well with 50 g. anhydrous sodium sulphate. Stand overnight and filter into the 1000 ml. conical flask.

Remove as much ether as possible from the extract by distillation on a water or steam bath, using the long water-cooled Liebig condenser.

Transfer the extract to the 250 ml. distillation flask closed by a cork carrying the thermometer reading to 200° C. and so fitted that the bottom of the capillary is level with the lower edge of the side tube. Attach to the air condenser and heat carefully on a sand bath or hot plate. When vigorous ebullition due to the ether has finished, replace the receiver by the wide 100 ml. beaker and continue heating until the extract again boils actively or until the thermometer indicates a temperature of 180° C. When cool, wash through the condenser with the bulk of the neutral oil and to this add the residue obtained by allowing the ether to evaporate from the distillate, in the 100 ml. beaker, for six hours at room temperature.

(*ii*) Distillation and Separation of Neutral Oil

Reagent

Dimethyl sulphate. See Appendix A, page 61. (To ensure freedom from acid the dimethyl sulphate should be shaken the day before use with excess of anhydrous sodium carbonate, from which it is filtered immediately before it is required.)

Apparatus

Standard distillation apparatus (*Standard Methods for Testing Tar and its Products*, 2nd Ed., 1938, Serial No. C.O. 3-38, page 270). In place of the Crow receivers it is convenient to use three graduated, pear-shaped, glass-stoppered separating funnels as described on page 25, T 5. Otherwise it is necessary to transfer the fractions to weighed separating funnels.

Method

Weigh each of the three receivers. Weigh accurately 100 g. $\pm$ 1 of the neutral oil in the F4 distillation flask and distil at the steady rate of 5 ml. $\pm$0.5 per minute (approximately 3 drops in 2 seconds) into the first receiver. When the thermometer indicates 230° C., remove the receiver and replace by the second receiver; substitute the third receiver when the thermometer indicates 290° C. Remove the third receiver as soon as the thermometer indicates 335° C., at which stage the distillation is stopped. Do not collect the drainings from the condenser with this fraction.

Determine the weight of each of the three fractions and treat each in the following manner:

If Crow receivers are used, pour the fraction into a weighed separating funnel of the type described on page 25. Wash out the Crow receiver with two successive amounts of dimethyl sulphate, each equal in volume to the

amount of oil in the receiver. Add these to the separating funnel and proceed with the determination of the weight of neutral oil insoluble in dimethyl sulphate.

If the graduated separating funnels are used, add to the fraction twice its volume of dimethyl sulphate and proceed with the determination of the weight of neutral oil insoluble in dimethyl sulphate.

The percentage of neutral oil soluble in dimethyl sulphate distilling at the specified temperatures is calculated thus:

If

N = neutral oil as per cent W/W of product

P = DMS insoluble neutral oil as per cent W/W neutral oil

T = DMS soluble neutral oil as per cent W/W neutral oil = 100 - P

X = DMS soluble neutral oil distilling below 230° C. as per cent W/W neutral oil

Y = DMS soluble neutral oil distilling from 230-290° C. as per cent W/W neutral oil

Z = DMS soluble neutral oil distilling from 290-335° C. as per cent W/W neutral oil

then

(T - X) N/100 = DMS soluble neutral oil distilling above 230° C. as per cent W/W product.

(T - X - Y) N/100 = DMS soluble neutral oil distilling above 290° C. as per cent W/W product

(T - X - Y - Z) N/100 = DMS soluble neutral oil distilling above 335° C. as per cent W/W product.

The method may be expected to give an accuracy of $\pm x$. This should be borne in mind when interpreting the results.

Interpret x as follows:

DMS soluble neutral oil distilling above 230° C. as per cent W/W product, $\pm$ 2.

DMS soluble neutral oil distilling above 290° C. as per cent W/W product, $\pm$ 1.

DMS soluble neutral oil distilling above 335° C. as per cent W/W product, $\pm$ 0.5.

Determination of Stability of the Undiluted Wash T 8

(a) *Miscible Tar Oil Winter Washes*

APPARATUS

A refrigerator maintained at - 10° C. $\pm$ 1° *or* a large vacuum flask

1 1500 ml. beaker 1 8-oz. white glass bottle

1 100 mesh sieve B.S. 410, 1943

METHOD

Place 200 ml. of the sample contained in the well-corked 8 oz. white glass bottle, in the refrigerator at - 10° C. $\pm$ 1° for 16 hours, or place the 8 oz. bottle, containing 200 ml. of the sample, in the centre of the vacuum flask surrounded by a freezing mixture capable of maintaining the temperature at - 10° C. $\pm$ 1°. (See Appendix B, p. 62.)

After 16 hours examine the cooled sample for cloudiness and crystalline deposit.

Warm to 0° C. and, without avoidable agitation, decant rapidly 75 ml. of the sample into 925 ml. ice-cooled distilled water in the 1500 ml. beaker, stirring the water vigorously. Allow to stand for 4 hours at room temperature.

Note the amount of oil separated.

Pour the emulsion through the 100 mesh B.S. sieve and note the deposit retained on the sieve.

The sample shall be considered to comply with the specification if

(*i*) after cooling, the undiluted wash shows no marked cloudiness or crystalline deposit, and

(*ii*) after standing at room temperature, the diluted wash shows no more than slight traces of oil separation, and

(*iii*) after pouring the diluted wash through the sieve, not more than very slight traces of crystalline or slimy deposit are retained.

(b) *Stock Emulsion Tar Oil Winter Washes*

APPARATUS

A refrigerator maintained at − 5° C. ± 1° *or* a large vacuum flask

1 wide necked 4 oz. white glass bottle
1 water bath
1 1500 ml. beaker
1 100 mesh sieve B.S. 410, 1943

METHOD

Place 75 ml. of the sample contained in the well-corked 4 oz. white glass bottle, in the refrigerator at − 5° C. ± 1° for 48 hours, or place the 4 oz. bottle, containing 75 ml. of the sample, in the centre of the vacuum flask surrounded by a freezing mixture capable of maintaining the temperature at − 5° C. ± 1°. (See Appendix C, p. 62.)

After 48 hours, examine the cooled sample for obvious separation of oil or sediment.

Place the bottle in the water bath at 20° C. ± 3° for one hour. Pour the contents into 825 ml. of distilled water at the same temperature, with vigorous stirring. Remove as much residual emulsion as possible from the bottle by rinsing with a further 100 ml. of distilled water at the same temperature, adding to the main bulk and maintaining the stirring during this operation. Allow to stand 4 hours at room temperature.

Note the amount of oil separated.

Restir the emulsion and pour through the 100 mesh B.S. sieve and note the deposit retained on the sieve.

The sample shall be considered to comply with the specification if

(*i*) after cooling, the undiluted wash shows no obvious separation of oil or sediment, and

(*ii*) after standing at room temperature, the diluted wash shows not more than slight traces of oil separation, and

(*iii*) after pouring the diluted wash through the sieve, not more than very slight traces of crystalline or slimy deposit are retained.

Determination of Stability of Diluted Wash T 9

REAGENT

Dissolve 1.85 g. calcium carbonate (A.R.) and 0.74 g. magnesium oxide (A.R.) in the minimum of dilute hydrochloric acid.

Expel the excess acid by evaporation to dryness on a water bath and dissolve the residue in 100 ml. water.

APPARATUS

1 1500 ml. beaker

1 100 mesh sieve B.S. 410, 1943

METHOD

To 915 ml. distilled water at room temperature add 10 ml. of the above stock solution of calcium and magnesium chlorides. This, when the sample is added, will give a solution containing calcium and magnesium chlorides in equimolecular proportions together equivalent to 40 parts of calcium carbonate per 100,000. Stir vigorously with a glass rod and add rapidly 75 ml. of the sample (at room temperature). Allow to stand for four hours and after gentle stirring pour the dilution through the 100 mesh B.S. sieve.

Note the amount of free oil retained on the sieve.

The sample shall be considered to comply with the specification if not more than slight traces of free oil are retained by the sieve.

Note. When special instructions for diluting the wash accompany the sample, prepare the hard water as above and carry out the dilution in the manner laid down for the particular wash, using 75 ml. per 925 ml. of the hard water.

PETROLEUM OIL WASHES

MISCIBLE PETROLEUM OIL WINTER WASHES

SPECIFICATION

The specification refers only to single phase products compounded from petroleum oils.

1. *Content of Neutral Oil*

The wash shall yield not less than 75 per cent by weight neutral oil when analysed by the prescribed method P 2.

2. *Content of Phenols*

Not more than 6 per cent by weight of the wash shall be phenols as determined by the prescribed method P 3.

3. *Specific Gravity*

The specific gravity of the isolated neutral oil shall be between 0.86 and 0.93 at 15.5° C./15.5° when determined by the prescribed method P 5.

4. *Volatility*

The amount of isolated neutral oil distilling at an oil temperature of 350° C. shall be not more than 5 per cent of its volume when determined by the prescribed method P 6.

5. *Unsulphonated Residue*

Not less than 65 per cent by volume of the total isolated neutral oil shall remain unsulphonated when treated in the prescribed manner P 8.

6. *Stability*

(*a*) The undiluted wash shall conform to the prescribed test for stability P 10 (a).

(*b*) The diluted wash shall conform to the prescribed test for stability P 11 (a).

STOCK EMULSION PETROLEUM OIL WINTER WASHES

SPECIFICATION

The specification refers only to polyphase products compounded from petroleum oils.

1. *Content of Neutral Oil*

The wash shall yield not less than 60 per cent by weight neutral oil when analysed by the prescribed method P 2.

2. *Specific Gravity*

The specific gravity of the isolated neutral oil shall be between 0.86 and 0.93 at 15.5° C./15.5° when determined by the prescribed method P 5.

3. *Volatility*

The amount of isolated neutral oil distilling at an oil temperature of 350° C. shall be not more than 5 per cent of its volume when determined by the prescribed method P 6.

4. *Unsulphonated Residue*

Not less than 65 per cent by volume of the total isolated neutral oil shall remain unsulphonated when treated in the prescribed manner P 8.

5. *Stability*

(*a*) The undiluted wash shall conform to the prescribed test for stability P 10 (b).

(*b*) The diluted wash shall conform to the prescribed test for stability P 11 (b).

STOCK EMULSION PETROLEUM OIL SUMMER WASHES FOR ORCHARD USE

SPECIFICATION

The specification refers to polyphase petroleum summer washes excluding products containing additional insecticidal or fungicidal material.

1. *Content of Neutral Oil*

The wash shall yield not less than 60 per cent by weight neutral oil when analysed by the prescribed method P 2.

2. *Specific Gravity*

The specific gravity of the isolated neutral oil shall be between 0.84 and 0.92 at 15.5° C./15.5° when determined by the prescribed method P 5.

3. *Distillation Range*

The neutral oil when extracted from the wash by the prescribed method P 7 shall have a distillation range such that :

the temperature at which 10 per cent of the oil has distilled shall lie between 310° C. and 340° C.,

the temperature at which 50 per cent of the oil has distilled shall lie between 350° C. and 375° C.,

the temperature at which 80 per cent of the oil has distilled shall lie between 380° C. and 400° C.

4. *Unsulphonated Residue*

Not less than 92 per cent by volume of the total isolated neutral oil shall remain unsulphonated when treated in the prescribed manner P 8.

5. *Viscosity*

The viscosity of the isolated neutral oil shall lie between 100 seconds and 200 seconds at 70° F. when determined by the prescribed method P 9.

6. *Stability*

(*a*) The undiluted wash shall conform to the prescribed test for stability P 10 (c).

(*b*) The diluted wash shall conform to the prescribed test for stability P 11 (c).

STOCK EMULSION PETROLEUM OIL SUMMER WASHES FOR GLASSHOUSE USE

SPECIFICATION

The specification refers to polyphase petroleum summer washes excluding products containing additional insecticidal or fungicidal material.

1. *Content of Neutral Oil*

The wash shall yield not less than 60 per cent by weight neutral oil when analysed by the prescribed method P 2.

2. *Specific Gravity*

The specific gravity of the isolated neutral oil shall be between 0.84 and 0.89 at 15.5° C./15.5° when determined by the prescribed method P 5.

3. *Distillation Range*

The neutral oil when extracted from the wash by the prescribed method P 7 shall have a distillation range such that:

the temperature at which 10 per cent of the oil has distilled shall lie between 310° C. and 340° C.,

the temperature at which 50 per cent of the oil has distilled shall lie between 350° C. and 375° C.,

the temperature at which 80 per cent of the oil has distilled shall lie between 380° C. and 400° C.

4 *Unsulphonated Residue*

Not less than 95 per cent by volume of the total isolated neutral oil shall remain unsulphonated when treated in the prescribed manner P 8.

5. *Viscosity*

The viscosity of the isolated neutral oil shall lie between 100 seconds and 200 seconds at 70° F. when determined by the prescribed method P 9.

6. *Stability*

(*a*) The undiluted wash shall conform to the prescribed test for stability P 10 (d).

(*b*) The diluted wash shall conform to the prescribed test for stability P 11 (d).

METHODS OF ANALYSIS*

Sampling P 1

The method of sampling will depend upon the circumstances and is to be based on Standard Methods for Testing Petroleum and its Products, 9th Ed., 1948, p. 344 *et seq.* The manufacturer's instructions, if any, for diluting the product should accompany the sample, which should not be less than one quart in volume.

Determination of Neutral Oil Content P 2

REAGENTS

- Sodium hydroxide solution (10 per cent W/W)
- Sodium hydroxide solution (1 per cent W/W)
- Ether (see Appendix D, p. 62)
- Sodium chloride solution (saturated)
- Anhydrous sodium sulphate
- Hydrochloric acid solution (4 per cent W/W)

APPARATUS

- 2 1500 ml. separating funnels
- 1 250 ml. separating funnel
- 1 filter funnel
- 1 Liebig condenser (not less than 30″ water jacket) and adapter
- 1 1000 ml. lipped beaker
- 1 2000 ml. conical flask
- 1 1500 ml. conical flask
- 1 200 ml. extraction flask
- 1 wash bottle of dry ether
- 1 splash head, with side inlet
- 1 water or steam bath
- 1 water or steam oven at 98°C. ±2
- 1 desiccator
- 1 ground glass plate

METHOD

Weigh accurately about 50 ml. of the well-stirred sample. Wash into the 1500 ml. separating funnel with 500 ml. of water. Add 100 ml. of 10 per cent sodium hydroxide solution and 500 ml. of ether. Shake and allow to stand until a clear ether layer has separated. If the emulsion has not broken sufficiently after standing overnight, add 10 ml., or more if necessary, of saturated sodium chloride solution and rotate gently until the emulsion breaks (See Notes 1 and 2).

Withdraw the lower layer into the second 1500 ml. separating funnel and to this add 200 ml. of ether and shake. After allowing to stand for one hour, withdraw the lower layer into the lipped beaker and add the ether layer to that from the first extraction which remains in the first separating funnel.

Return the alkaline layer to the empty separating funnel and repeat its extraction with 200 ml. lots of ether, until a drop of the ether washings when allowed to evaporate from the cleaned ground glass plate no longer leaves a continuous film of oil. Add the ether washings to the first separating funnel and wash three times with successive 50 ml. lots of 1 per cent sodium hydroxide solution. Wash once with 100 ml. of distilled water.

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* In drawing up the methods of analysis, it has been considered desirable to adopt the distillation technique specified in *Standard Methods for Testing Tar and its Products* (S.T.P.T.C. 2nd ed., 1938; Revised section 7, 1943, p. 203) in preference to that specified by the American Society for Testing Materials (A.S.T.M.: D. 447/41) because most manufacturers of petroleum oil washes in this country normally use the S.T.P.T.C. technique and because it is adopted for the analysis of mixed tar-petroleum washes. It has been determined that, over the range covered by the specifications, the A.S.T.M. method gives results which are about 12°C lower than those given by the S.T.P.T.C. method.

Only emulsifying agents at present in common use in Great Britain have been taken into consideration. If new emulsifiers are introduced, it may be necessary at some future date to review and augment the specifications and methods of analysis.

Combine and reserve the washings and alkaline layer in the lipped beaker for Determination of Phenols Content P 3.

Wash the combined ether layers once with 100 ml. of 4 per cent hydrochloric acid. Transfer the acid layer to the 250 ml. separating funnel and wash twice with 50 ml. lots of ether. Reject the acid layer.

Add the ether washings to the main bulk of the ether extract in the first separating funnel and wash once with 100 ml. of water. Reject the aqueous washings. Transfer the ether solution to the large conical flask and concentrate to 250-300 ml. on the water bath, distilling the ether through the water-cooled Liebig condenser. When cool, transfer to a dry flask, shake well with 20 g. of anhydrous sodium sulphate and allow to stand overnight.

Filter the ether solution through an open-textured filter paper, collecting the first 100 ml. of the filtrate in the tared extraction flask and the remainder in another flask. Transfer the residual sodium sulphate from the conical flask to the filter paper by means of successive 50 ml. lots of ether (previously dried over anhydrous sodium sulphate) and finally wash the residue and filter paper with dry ether from a wash bottle until a drop of the ether washings when allowed to evaporate from the cleaned ground glass plate no longer leaves a continuous film of oil.

Distil the ether from the first 100 ml. of the filtrate on the water or steam bath, using the water-cooled Liebig condenser to which the extraction flask is attached by way of the splash head. Add the combined washings and remainder of the filtrate to the residue in the extraction flask at suitable stages. This may be done, if convenient, by means of a suitable separating funnel, the delivery tube of which is inserted through the cork of the extraction flask.

Remove the last traces of ether by heating the flask in the oven at 98° C. $\pm$ 2 to constant weight, displacing the ether vapour by a puff of air from the bellows at intervals.

Transfer the flask to the desiccator, reweigh when cool, and calculate the percentage W/W of neutral oil in the wash.

The method may be expected to give an accuracy of $\pm$ 2. This should be borne in mind when interpreting the results.

Note 1. *Miscible Petroleum Oil Washes.* In the case of certain emulsions in which resin soaps are employed, the emulsion is easily broken by washing the sample into the separating funnel with the 500 ml. ether followed by the addition of the sodium hydroxide solution and the water.

Certain emulsifiers are relatively insoluble in 2 per cent sodium hydroxide solution, and are not removed by either procedure. Such emulsifiers are detected by the formation of a definite intermediate layer during ether extraction or by the formation of an emulsion when one or two drops of the extracted oil are shaken with 5 ml. water. The extraction must then be repeated using amounts of sodium hydroxide solution to give a concentration of not more than 0.1 per cent in the aqueous phase. The combined ether extracts are finally extracted with 1 per cent sodium hydroxide and the analysis is continued as above, starting from " wash once with 100 ml. of distilled water " (end of paragraph 3).

Note 2. *Stock Emulsion Petroleum Oil Washes.* Certain emulsions are not completely broken after a short period by this alkaline treatment. A partial separation of either the ether or the aqueous layer is obtained. By withdrawing the clear phase and replacing with water or ether, according to the phase removed, a complete separation is eventually obtained.

Determination of Phenols Content P 3

REAGENTS

- Barium hydroxide (A.R.)
- Hydrochloric acid (A.R. 32 per cent W/W)
- Barium chloride solution (10 per cent W/V)
- Ether (see Appendix D, p. 62)
- Anhydrous sodium sulphate

APPARATUS

- 1 2000 ml. conical flask
- 1 Buchner funnel with 2000 ml. filter flask.
- 1 200 ml. extraction flask
- 1 Liebig condenser (not less than 30″ water jacket) and adapter
- 1 vacuum desiccator
- 2 1500 ml. separating funnels
- 1 beaker (not less than 2000 ml. capacity)
- 1 splash head, with side inlet
- 1 water or steam bath
- 1 ground glass plate

METHOD

Transfer the combined alkaline layers and washings from the Determination of Neutral Oil Content P 2 to the large conical flask and remove dissolved ether by distillation until the solution begins to form a persistent froth. Cool somewhat, pour carefully into the large beaker containing 10 g. of solid barium hydroxide. Place on the boiling water bath and stir until the precipitate has coagulated. Test for complete precipitation of soaps by the non-formation of precipitate on the addition of a few drops of barium chloride solution. Filter hot through the Buchner funnel with suction and wash the precipitate with three successive 50 ml. lots of hot water.

Add 1-2 ml. of 0.1 per cent methyl orange solution to the filtrate and acidify with concentrated hydrochloric acid. When cold, transfer to the separating funnel, shake with 100 ml. of ether and allow to stand one hour. Withdraw the aqueous layer to the second separating funnel and extract with successive 100 ml. lots of ether until a drop of the ether washings when allowed to evaporate from the cleaned ground glass plate no longer leaves a continuous film of oil.

Unite the ether washings and the ether extract in the first separating funnel and wash once with 100 ml. of distilled water. Transfer to a dry flask, shake well with 10 g. of anhydrous sodium sulphate and allow to stand overnight.

Filter the ether solution through an open-textured filter paper, collecting the first 100 ml. of the filtrate in the tared extraction flask and the remainder in another flask. Transfer the residual sodium sulphate from the conical flask to the filter paper by means of successive 50 ml. lots of ether (previously dried over anhydrous sodium sulphate) and finally wash the residue and filter paper with dry ether from a wash bottle until a drop of the ether washings when allowed to evaporate from the cleaned ground glass plate no longer leaves a continuous film of oil.

Distil the ether from the first 100 ml. of the filtrate on the water or steam bath, using the water-cooled Liebig condenser to which the extraction flask is attached by way of the splash head. Add the combined washings and remainder of the filtrate to the residue in the extraction flask at suitable stages. This may be done, if convenient, by means of a suitable separating funnel, the delivery tube of which is inserted through the cork of the extraction flask.

To remove the last traces of ether, transfer the flask to a vacuum desiccator and exhaust for 30 minutes. Leave the flask under vacuum in the desiccator for an additional hour. Reweigh and calculate the percentage (W/W) of phenols in the wash.

The method may be expected to give an accuracy of ± 1. This should be borne in mind when interpreting the results.

Recovery of Neutral Oil for Analysis P 4

REAGENTS

- Sodium hydroxide solution (50 per cent W/W)
- Hydrochloric acid (4 per cent W/W)
- Ether (see Appendix D, p. 62)
- Anhydrous sodium sulphate
- Sodium chloride solution (saturated)

APPARATUS

- 2 separating funnels (not less than 2000 ml. capacity)
- 1 separating funnel (250 ml. capacity)
- 1 Liebig condenser (not less than 30″ water jacket) and adapter
- 1 wide 100 ml. beaker
- 1 splash head, with side inlet
- 1 1000 ml. conical flask
- 1 water or steam bath
- 1 thermometer (0-200° C.)
- 1 500 ml. distillation flask
- 1 air condenser (type 3, B.S.658, 1936)

METHOD

Transfer to the first large separating funnel approximately 300 ml. of the sample, 1000 ml. of distilled water and 500 ml. of ether. Add at least 10 ml. of the sodium hydroxide solution and, if necessary, saturated sodium chloride solution in amounts found by previous experience (under Determination of Neutral Oil Content) to be required to break the emulsion.

When a satisfactory separation of aqueous and ether layers has been obtained, transfer the aqueous layer to the second separating funnel and extract with three successive 200 ml. lots of ether.

Unite all the ether extracts in the first separating funnel and wash once with 200 ml. of distilled water. Reject this wash water and all ether-extracted alkaline layers.

Wash the combined ether layers once with 100 ml. of 4 per cent hydrochloric acid. Transfer the acid layer to the 250 ml. separating funnel and wash twice with 50 ml. lots of ether. Reject the acid layer.

Add the ether washings to the main bulk of the ether extracts in the first separating funnel and wash once with 100 ml. of water. Reject the aqueous washings. Concentrate the ether solution to 400-600 ml. on the water bath, distilling the ether through the water-cooled Liebig condenser. Cool the concentrated ether solution, transfer to a dry flask and shake well with 50 g. of anhydrous sodium sulphate. Stand overnight and filter into the 1000 ml. conical flask.

Remove as much ether as possible from the extract by distillation on a water or steam bath, using the water-cooled Liebig condenser.

Transfer the extract to the 500 ml. distillation flask and close by a cork carrying the thermometer, so fitted that the bottom of the capillary is level with the lower edge of the side tube. Attach to the air condenser and heat carefully on a sand bath or hot plate. When vigorous ebullition due to

the ether has finished, replace the receiver by the wide 100 ml. beaker and continue heating until the extract again boils actively or until the thermometer indicates a temperature of 180° C. When cool, wash through the condenser with the bulk of the neutral oil and to this oil add any residue obtained by allowing the ether to evaporate from the distillate in the 100 ml. beaker for at least six hours at room temperature.

Determination of Specific Gravity of Neutral Oil P 5

APPARATUS

1 50 ml. British Standard Density Bottle B.S. 733, 1937
1 water bath at 15.5° C.

METHOD

Fill the tared bottle with distilled water at about 16° C. and place in a water bath maintained at 15.5° C. for 5 minutes. Replace the stopper and wipe the top, remove the bottle from the water bath, wipe the adhering water from the sides of the bottle and weigh. Let W_w be the weight of water required to fill the bottle at 15.5° C. Repeat this procedure using the oil under test in place of water. Let W_o be the weight of oil required to fill the bottle at 15.5° C.

$$\text{Specific gravity at } 15.5°\text{C./}15.5° = \frac{W_o}{W_w}$$

Determination of Volatility of Neutral Oil P 6

APPARATUS

A standard distillation flask (Schedule F 4, *Standard Methods for Testing Tar and its Products*, S.T.P.T.C., 2nd Ed., 1938, p. 365) held in a vertical position by a clamp at the extreme upper end of the neck

A standard thermometer having a range of 90° to 400° C. (Schedule No. T4a—S.T.P.T.C.)

A standard draught screen (Schedule No. S3—S.T.P.T.C.) from which the shelf has been removed

A standard air condenser (Schedule No. C3—S.T.P.T.C.). The side arm of the flask shall extend at least 25 mm. beyond the cork in the upper end of the condenser

1 100 ml. Crow receiver

1 approx. 2″ length of thin-walled capillary tubing (as used for m.p. determinations)

METHOD

(a) *Preliminary Examination*

Transfer to the distillation flask 25 ml. neutral oil, add the short length of capillary tubing and replace the flask in position in the apparatus.

Fit the thermometer by means of a cork into the neck of the flask so that the mercury bulb is just clear of the bottom of the flask.

Using the naked flame of the burner, heat the oil so that the temperature recorded by the thermometer increases, above 250° C., at a rate of 5° C. in 30 seconds ± 10.

Note the number of drops of distillate which fall from the side arm of the flask before the thermometer reads 350° C. If this number is not more than two, the amount of oil distilling at an oil temperature of 350° C. does not exceed 5 per cent by volume. If this number is greater than two, the volatility of the oil must be determined by method (b).

(b) *Full Method*

Recover a sufficient amount of oil by the prescribed method P 4 to permit the weighing into the distillation flask of an amount equal to 100 ml. Add the short length of capillary tubing and replace the flask in position in the apparatus.

Fit the thermometer by means of a cork into the neck of the flask so that the mercury bulb is below the surface of the oil, the bottom of the capillary thread being level with that surface.

Using the naked flame of the burner, heat the oil so that the temperature recorded by the thermometer increases, above 250° C., at a rate of 5° C. in 30 seconds $\pm$ 10.

When the thermometer reads 350° C., remove the Crow receiver and record the volume of distillate collected.

Determination of Distillation Range of Neutral Oil P 7

APPARATUS

A standard distillation flask (Schedule F 4, *Standard Methods for Testing Tar and its Products*, S.T.P.T.C., 2nd Ed., 1938, p. 365) held in a vertical position by a clamp at the extreme upper end of the neck

A standard thermometer having a range of 90° to 400° C. (Schedule No. T4a—S.T.P.T.C.) so fitted into the flask that the bottom of the capillary tube is level with the lower edge of the side arm joint and the immersion mark is level with the top of the cork

A standard draught screen (Schedule No. S3—S.T.P.T.C.) from which the shelf has been removed

A standard air condenser (Schedule No. C3—S.T.P.T.C.). The side arm of the flask shall extend at least 25 mm. beyond the cork in the upper end of the condenser

1 100 ml. Crow receiver

METHOD

Weigh into the distillation flask an amount of neutral oil equal to 100 ml. and replace the flask in position in the apparatus.

Using the naked flame of the burner heat the oil until it begins to distil. Adjust the rate of distillation to 5 ml. $\pm$ 0.5 per minute.

Record the thermometer readings when 10 ml., 50 ml. and 80 ml. have distilled.

Determination of Unsulphonated Residue of Neutral Oil P 8

REAGENTS

Sulphuric acid 98.6 per cent $\pm$ 0.1 H_2SO_4

Sulphuric acid, pure, concentrated, sp. gr. 1.84

(See Appendix E, page 62, for details of preparation and standardization of sulphuric acid.)

APPARATUS

2 Fifty Per Cent—9 gramme Babcock Bottles for Testing Cream, B.S. 755, 1937

1 5 ml. pipette

1 50 ml. burette graduated in 0.1 ml. divisions

1 water bath, to take 2 test bottles (see Note 1)

A centrifuge capable of rotating test bottles of 165 mm. overall height at 1000-1250 r.p.m. and provided with a protecting cover and shield approximately 2 ft. in diameter. (See Note 2.)

METHOD

Introduce with the pipette about 5 ml. of neutral oil into a tared, thoroughly clean, dry test bottle and weigh. Add slowly from the burette 20 ml. of 98.6 per cent sulphuric acid in four equal portions, washing down any oil remaining in the neck. Shake the bottle rapidly for ten seconds after each addition of acid. Cool, if necessary, to keep the temperature below 60° C. Immerse the bottle, lightly stoppered with a rubber bung, in the boiling water bath for one hour, clamping it in a vertical position with the bulb completely submerged. (See Note 1.) Remove the bottle from the bath at 10 minute intervals, shake for 10 seconds and replace. Take out the bottle after one hour and add sufficient sulphuric acid, sp. gr. 1.84, to bring the oil into the graduated portion of the neck. Place the bottle in the centrifuge and counter-poise, preferably with the second bottle in which a duplicate determination is being simultaneously carried out. Centrifuge for 5 minutes at 1000-1250 r.p.m. (see Note 2), take out, cool to 15° C. and read the volume of oil as accurately as possible with the help of a lens (1 division = 0.05 ml.). Centrifuge again, until the volume of oil is constant.

$$\%\ \text{unsulphonated residue v/v} = \frac{\text{vol. of oil read} \times \text{sp. gr. of oil taken} \times 100}{\text{wt. of oil taken}}$$

Notes:

1. An oil bath or steam oven maintained at 98° C. ± 2 may be used in place of the water bath.

2. Centrifuges with lower speeds can be used, but the period of rotation may have to be increased until a constant reading of the volume of oil is obtained.

3. If the unsulphonated oil layer is so dark that the line of demarcation between oil and acid is not clearly visible, a few drops of water should be added to form an intermediate layer, when the volume can be read after a few minutes' standing. This procedure tends to give slightly higher results.

4. Duplicate results should agree within 2 per cent, based on the neutral oil.

5. The sulphuric acid reagent should be carefully standardized, as slight variations in strength from 98.6 per cent affect the result substantially. The strength of the acid should be checked not more than 24 hours before each determination is carried out.

Determination of Viscosity of Neutral Oil P 9

APPARATUS

A Redwood No. 1 viscometer (*Standard Method for Testing Petroleum and its Products*, 9th Ed., 1948, p. 509).

A 50 ml. Kohlrausch flask, B.S. 615, 1936

A stop-watch

METHOD

Clean the oil cup of the viscometer with a suitable solvent and dry thoroughly to remove all traces of the solvent. Any material used for rubbing the interior of the oil cup or for cleaning the jet, shall not be such as will disintegrate in use, leaving particles which may interfere with the free flow of the sample through the jet. Set up and level the apparatus.

Heat about 200 ml. of the sample in a separate vessel to within a few degrees of 70° F. Either water or oil may be used in the heating bath; the level of the heating liquid shall be at least 10 mm. below the rim of the

cup. Heat the bath of the viscometer to a few degrees above 70° F. and pour the oil into the oil cup. Adjust the temperature of the bath until the temperature of the oil in the cup is maintained at 70° F.; gently rotate the stirrer in the bath at frequent intervals or (preferably) continuously. Stir the oil gently during the preliminary period, but do not stir during the actual test. When the oil has reached a steady temperature of 70° F., adjust the oil level by allowing the oil to flow out until the surface of the oil touches the filling-point. Place the oil cup cover in position. Place the Kohlrausch flask centrally below the jet and adjust the top of the neck of the flask to within a few millimetres of the under side of the jet. Do not insulate the flask in any way. Lift the valve and start a stop watch simultaneously. Stop the watch when the oil reaches the graduation mark on the flask. Record the interval in seconds between the two readings of the stop-watch as the viscosity of the sample.

The above method is based on the Method, Serial Designation IP-70/46, *Standard Methods for Testing Petroleum and its Products,* 9th Ed., 1948, p. 516; the procedure described in this latter method (which includes a number of additional precautions to be taken) should be used for official determinations of Redwood viscosities.

Determination of Stability of Undiluted Wash P 10

APPARATUS

A refrigerator maintained at −5° C. ± 1 *or* a large vacuum flask
1 1500 ml. beaker 1 water bath
1 8 oz. white glass bottle *or* 1 wide necked 4 oz. white glass bottle

METHOD

(a) *Miscible Petroleum Oil Winter Washes*

Place 200 ml. of the sample, contained in the well-corked 8 oz. white glass bottle, in the refrigerator at −5° C. ± 1 for 48 hours; *or* place the 8 oz. bottle containing 200 ml. of the sample in the centre of the vacuum flask surrounded by a freezing mixture capable of maintaining the temperature at −5° C. ± 1. (See Appendix C, page 62.)

After 48 hours examine the cooled sample for cloudiness.

Warm to 0° C. and, without avoidable agitation, decant rapidly 75 ml. of the sample into 925 ml. ice-cooled distilled water in the 1500 ml. beaker, stirring the water vigorously. Allow to stand for 4 hours at room temperature.

Note the amount of oil separated.

The sample shall be considered to comply with the specification if

(*i*) after cooling, the undiluted wash shows no marked cloudiness, and

(*ii*) after standing at room temperature, the diluted wash shows no more than slight traces of oil separation.

(b) *Stock Emulsion Petroleum Oil Winter Washes*

Place 75 ml. of the sample, contained in the well-corked 4 oz. white glass bottle, in the refrigerator at −5° C. ± 1 for 48 hours, *or* place the 4 oz. bottle, containing 75 ml. of the sample, in the centre of the vacuum flask surrounded by a freezing mixture capable of maintaining the temperature at −5° C. ± 1. (See Appendix C, page 62.)

After 48 hours, examine the cooled sample for separation of free oil.

Place the bottle in the water bath at 20° C. ±3 for one hour. Pour the contents into 825 ml. of distilled water at the same temperature with

vigorous stirring. Remove as much residual emulsion as possible from the bottle by rinsing with a further 100 ml. of distilled water at the same temperature, adding to the main bulk and maintaining the stirring during this operation. Allow to stand 4 hours at room temperature.

Note the amount of oil separated.

The sample shall be considered to comply with the specification if

(*i*) after cooling, the undiluted wash shows no obvious separation of oil, and

(*ii*) after standing at room temperature, the diluted wash shows not more than slight traces of oil separation.

(c) *Stock Emulsion Petroleum Oil Summer Washes for Orchard Use*

Apply the method shown under (b) above.

(d) *Stock Emulsion Petroleum Oil Summer Washes for Glasshouse Use*

Apply the method shown under (b) above.

Determination of Stability of Diluted Wash P 11

REAGENT

Dissolve 1.85 g. of calcium carbonate (A.R.) and 0.74 g. of magnesium oxide (A.R.) in the minimum of dilute hydrochloric acid.

Expel the excess acid by evaporation to dryness on a water bath and dissolve the residue in 100 ml. of water.

APPARATUS

1 1000 ml. beaker.

METHOD

(a) *Miscible Petroleum Oil Winter Washes*

To 940 ml. of distilled water at room temperature add 10 ml. of the above stock solution of calcium and magnesium chlorides. This, when the sample is added, gives a solution containing calcium and magnesium chlorides in equimolecular proportions together equivalent to 40 parts of calcium carbonate per 100,000. Stir vigorously with a glass rod and add rapidly 50 ml. of the sample (at room temperature). Allow to stand for 4 hours. Note the amount of free oil separated.

The sample shall be considered to comply with the specification if not more than slight traces of free oil have separated.

(b) *Stock Emulsion Petroleum Oil Winter Washes*

To 940 ml. of distilled water at room temperature add 10 ml. of the above stock solution of calcium and magnesium chlorides. This, when the sample is added, gives a solution containing calcium and magnesium chlorides in equimolecular proportions together equivalent to 40 parts of calcium carbonate per 100,000. Add 50 ml. of the sample to 50 ml. of the prepared hard water and mix thoroughly. Add the mixture rapidly to the remaining hard water (at room temperature) stirring vigorously with a glass rod. Allow to stand for 4 hours. Note the amount of free oil separated.

The sample shall be considered to comply with the specification if not more than slight traces of free oil have separated.

(c) *Stock Emulsion Petroleum Oil Summer Washes for Orchard Use*

Apply the method shown under (b) above, using 970 ml. of distilled water, 10 ml. stock solution and 20 ml. emulsion.

(d) *Stock Emulsion Petroleum Oil Summer Washes for Glasshouse Use*

Apply the method shown under (b) above, using 980 ml. distilled water, 10 ml. stock solution and 10 ml. emulsion.

Note. When special instructions for diluting the wash accompany the sample, prepare the hard water as above and carry out the dilution in the manner laid down for the particular wash.

TAR-PETROLEUM OIL WASHES

MISCIBLE TAR-PETROLEUM OIL WINTER WASHES

SPECIFICATION

The specification is intended to apply to tar-petroleum oil winter washes in which the petroleum oil content is of the order of twice the neutral tar oil content.

1. *Content of Total Neutral Oil*

The wash shall yield not less than 75 per cent by weight total neutral oil when analysed by the prescribed method TP 2.

2. *Content of Phenols*

Not more than 7 per cent by weight of the wash shall be phenols when determined by the prescribed method TP 3.

3. *Content of Neutral Oil Soluble and Insoluble in Dimethyl Sulphate*

(*a*) Not less than 30 per cent by weight of the total neutral oil shall be soluble in dimethyl sulphate when determined by the prescribed method TP 4.

(*b*) Not less than 60 per cent by weight of the total neutral oil shall be insoluble in dimethyl sulphate when determined by the prescribed method TP 4.

4. *Distillation Range*

The neutral oil when extracted from the wash by the prescribed method TP 5 shall have a distillation range such that

not more than 10 per cent by weight of the neutral oil shall have distilled at 290° C.

not more than 50 per cent by weight of the neutral oil shall have distilled at 340° C.

not more than 80 per cent by weight of the neutral oil shall have distilled at 375° C.

5. *Unsulphonated Residue*

Not less than 65 per cent by volume of the neutral oil insoluble in dimethyl sulphate shall remain unsulphonated when treated by the prescribed method TP 6.

6. *Stability*

(*a*) The undiluted wash shall conform to the prescribed test for stability TP 7.

(*b*) The diluted wash shall conform to the prescribed test for stability TP 8.

STOCK EMULSION TAR-PETROLEUM OIL WINTER WASHES

SPECIFICATION

The specification is intended to apply to tar-petroleum oil winter washes in which the petroleum oil content is of the order of twice the neutral tar oil content.

1 *Content of Total Neutral Oil*

The wash shall yield not less than 60 per cent by weight total neutral oil when analysed by the prescribed method TP 2.

2. *Content of Phenols*

Not more than 3 per cent by weight of the wash shall be phenols when determined by the prescribed method TP 3.

3. *Content of Neutral Oil Soluble and Insoluble in Dimethyl Sulphate*

(*a*) Not less than 30 per cent by weight of the total neutral oil shall be soluble in dimethyl sulphate when determined by the prescribed method TP 4.

(*b*) Not less than 60 per cent by weight of the total neutral oil shall be insoluble in dimethyl sulphate when determined by the prescribed method TP 4.

4 *Distillation Range*

The neutral oil when extracted from the wash by the prescribed method TP 5 shall have a distillation range such that

not more than 10 per cent by weight of the neutral oil shall have distilled at 290° C.

not more than 50 per cent by weight of the neutral oil shall have distilled at 340° C.

not more than 80 per cent by weight of the neutral oil shall have distilled at 375° C.

5. *Unsulphonated Residue*

Not less than 65 per cent by volume of the neutral oil insoluble in dimethyl sulphate shall remain unsulphonated when treated by the prescribed method TP 6.

6. *Stability*

(*a*) The undiluted wash shall conform to the prescribed test for stability TP 7.

(*b*) The diluted wash shall conform to the prescribed test for stability TP 8.

METHODS OF ANALYSIS

Sampling TP 1

The method of sampling will depend upon the circumstances and is to be based on B.S. 616, 1938, *Sampling of Coal Tar and its Products*, or *Standard Methods for Testing Tar and its Products*, 2nd Ed., 1938, page 13 *et seq.*, and *Standard Methods of Testing Petroleum and its Products*, 9th Ed., 1948, page 344 *et seq.* The manufacturer's instructions, if any, for diluting the product should accompany the sample, which should not be less than one quart in volume.

Determination of Neutral Oil Content TP 2

Reagents

Sodium hydroxide solution (10 per cent W/W)
Sodium hydroxide solution (1 per cent W/W)
Ether (see Appendix D, p. 62)
Sodium chloride solution (saturated)
Anhydrous sodium sulphate
Hydrochloric acid solution (4 per cent W/W)

Apparatus

2 1500 ml. separating funnels
1 250 ml. separating funnel
1 filter funnel
1 Buchner funnel with filter flask
1 Liebig condenser (not less than 30″ water jacket) and adapter
1 desiccator
1 200 ml. extraction flask
1 1000 ml. lipped beaker
1 2000 ml. conical flask
1 1500 ml. conical flask
1 wash bottle of dry ether
1 splash head with side inlet
1 water or steam bath
1 hot water or steam oven at 98° C. ± 2°
1 ground glass plate

Method

Weigh accurately about 50 ml. of the well-stirred sample. Wash into the 1500 ml. separating funnel with 500 ml. water. Add 100 ml. of 10 per cent sodium hydroxide solution and 500 ml. of ether. Shake and allow to stand until a clear ether layer has separated. If the emulsion has not broken sufficiently after standing overnight, add 10 ml., or more if necessary, of saturated sodium chloride solution and rotate gently until the emulsion breaks. (See Notes 1 and 2.)

Withdraw the lower layer into the second 1500 ml. separating funnel and to this add 200 ml. of ether and shake. After allowing to stand for one hour, withdraw the lower layer into the lipped beaker and add the ether layer to that from the first extraction which remains in the first separating funnel.

Return the alkaline layer to the empty separating funnel and repeat its extraction with 200 ml. lots of ether until a drop of the ether washings when allowed to evaporate from the cleaned ground glass plate no longer leaves a continuous film of oil. Add the ether washings to the first separating funnel and wash with successive 50 ml. lots of 1 per cent sodium hydroxide solution until the aqueous layer is almost colourless (3 or 4 washings are usually required). Wash once with 100 ml. of distilled water. Combine and reserve the washings and alkaline layer in the beaker for Determination of Phenols Content TP 3.

Extract the combined ether layers with successive 100 ml. lots of 4 per cent hydrochloric acid until the acid layer is lighter in colour than 0.001N aqueous iodine solution. If, as usually occurs, much carbonaceous matter is precipitated by the acid treatment, it may be convenient to filter by means of a filter pump at this stage and to wash the sludge with ether and reject the residue.

Unite the acid layers, transfer to the second separating funnel and wash twice with 50 ml. lots of ether. (The carbonaceous sludge, if not already removed, is usually held by the ether layer. To secure a good separation it may be convenient to add small amounts (20 ml.) of distilled water after the bulk of the acid layer has been withdrawn.)

Reject the acid layer.

Add the ether washings to the main bulk of the ether extract in the first separating funnel and wash once with 100 ml. water. Reject the aqueous washing. Transfer the ether solution to the large conical flask and concentrate to 250-300 ml. on the water bath, distilling the ether through the water-cooled Liebig condenser. When cool, transfer to a dry flask, shake well with 20 g. anhydrous sodium sulphate and allow to stand overnight.

Filter the ether solution through an open-textured filter paper, collecting the first 100 ml. of the filtrate in the tared extraction flask and the remainder in another flask. Transfer the residual sodium sulphate from the conical flask to the filter paper by means of successive 50 ml. lots of ether (previously dried over anhydrous sodium sulphate) and finally wash the residue and filter paper with dry ether from a wash bottle until a drop of the ether washings when allowed to evaporate from the cleaned ground glass plate no longer leaves a continuous film of oil.

Distil the ether from the first 100 ml. of the filtrate on the water or steam bath, using the water-cooled Liebig condenser to which the extraction flask is attached by way of the splash head. Add the combined washings and remainder of the filtrate to the residue in the extraction flask at suitable stages. This may be done if convenient by means of a suitable separating funnel, the delivery tube of which is inserted through the cork of the extraction flask.

Remove the last traces of ether by heating the flask in the oven at 98° C. $\pm$ 2° for two hours, displacing the ether vapour by a puff of air from the bellows at intervals.

Transfer the flask to the desiccator, reweigh when cool, and calculate the percentage (W/W) of neutral oil in the wash. The method may be expected to give an accuracy of $\pm$ 2. This should be borne in mind when interpreting the results.

Note (1). *Miscible Tar-Petroleum Oil Washes.* In the case of certain emulsions in which resin soaps are employed the emulsion is easily broken by washing the sample into the separating funnel with the 500 ml. of ether followed by the addition of the sodium hydroxide solution and the water.

Certain emulsifiers are relatively insoluble in 2 per cent sodium hydroxide solution and are not removed by either procedure. Such emulsifiers are detected by the formation of a definite intermediate layer during ether extraction or by the formation of an emulsion when one or two drops of the extracted oil are shaken with 5 ml. of water. The extraction must then be repeated using amounts of sodium hydroxide solution to give a concentration of not more than 0.1 per cent in the aqueous phase. The combined ether extracts are finally extracted with 1 per cent sodium hydroxide and the analysis is continued as above, starting from "Wash once with 100 ml. of distilled water" (para. 3).

Note (2). *Stock Emulsion Tar-Petroleum Oil Washes.* Certain emulsions are not completely broken after a short period by this alkaline treatment. A partial separation of either the ether or the aqueous layer is obtained. By withdrawing the clear phase and replacing with water or ether, according to the phase removed, a complete separation is eventually obtained.

Determination of Phenols Content TP 3

REAGENTS

Barium hydroxide (A.R.)
Hydrochloric acid (A.R. 32 per cent W/W).
Barium chloride solution (10 per cent W/V)
Ether (see Appendix D, p. 62)
Anhydrous sodium sulphate

APPARATUS

1 2000 ml. conical flask
1 Buchner funnel with 2000 ml. filter flask
1 200 ml. extraction flask
1 Liebig condenser (not less than 30″ water jacket) and adapter
2 1500 ml. separating funnels
1 beaker (not less than 2000 ml. capacity)
1 splash head with side inlet
1 water or steam bath
1 vacuum desiccator
1 ground glass plate

METHOD

Transfer the combined alkaline layers and washings reserved from the Determination of Neutral Oil Content TP 2 to the large conical flask and remove dissolved ether by distillation until the solution begins to form a persistent froth. Cool somewhat and pour carefully into the large beaker containing 10 g. solid barium hydroxide. Place on the boiling water bath and stir until the precipitate has coagulated. Test for complete precipitation of soaps by the non-formation of precipitate on the addition of a few drops of barium chloride solution. Filter hot through the Buchner funnel with suction and wash the precipitate with three successive 50 ml. lots of hot water. Acidify with concentrated hydrochloric acid. When cold, transfer to the separating funnel, shake with 100 ml. ether and allow to stand one hour. Withdraw the aqueous layer to the second separating funnel and extract with successive 100 ml. lots of ether (3 or 4 extractions are usually sufficient) until a drop of the ether washings when allowed to evaporate from the cleaned ground glass plate no longer leaves a continuous film of oil.

Unite the ether washings and the ether extract in the first separating funnel and wash once with 100 ml. distilled water. Transfer to a dry flask, shake well with 10 g. anhydrous sodium sulphate and allow to stand overnight.

Filter the ether solution through an open-textured filter paper, collecting the first 100 ml. of the filtrate in the tared extraction flask and the remainder in another flask. Transfer the residual sodium sulphate from the conical flask to the filter paper by means of successive 50 ml. lots of ether (previously dried over anhydrous sodium sulphate) and finally wash the residue and filter paper with dry ether from a wash bottle until a drop of the ether washings when allowed to evaporate from the cleaned ground glass plate no longer leaves a continuous film of oil.

Distil the ether from the first 100 ml. of the filtrate on the water or steam bath, using the water-cooled Liebig condenser to which the extraction flask is attached by way of the splash head. Add the combined washings and remainder of the filtrate to the residue in the extraction flask at suitable stages. This may be done, if convenient, by means of a suitable separating funnel, the delivery tube of which is inserted through the cork of the extraction flask.

To remove the last traces of ether transfer the flask to a vacuum desiccator and exhaust for 30 minutes. Leave the flask under vacuum in the desiccator for an additional hour. Reweigh and calculate the percentage (W/W) of phenols in the wash.

The method may be expected to give an accuracy of ± 1. This should be borne in mind when interpreting the results.

Determination of Neutral Oil Soluble and Insoluble in Dimethyl Sulphate

REAGENT **TP 4**

Dimethyl sulphate—see Appendix A, page 61. (To ensure freedom from acid, the dimethyl sulphate should be shaken the day before use with excess

of anhydrous sodium carbonate, from which it is filtered immediately before it is required).

APPARATUS

A pear-shaped, glass-stoppered separating funnel of 150 ml. capacity with delivery tube cut as short as possible and ground at right angles to the axis. Alternatively, the delivery jet may have a capillary bore equal in diameter to that of the tap. A wire is attached to the funnel, in such a manner that the funnel can be weighed on an ordinary analytical balance.

Manipulation is greatly facilitated if the funnel is graduated from the closed tap from 0-150 ml.

METHOD

Pour into the weighed separating funnel a known volume of about 30 ml. of the neutral oil and reweigh the funnel and oil. Add to the oil twice its volume of dimethyl sulphate, shake thoroughly, release the stopper and allow the funnel to stand upright overnight at room temperature.

Withdraw the lower layer slowly until the interface is at the bottom of the tap bore. Remove traces of the dimethyl sulphate layer from the delivery tube by means of a roll of filter paper. If the bore of the delivery tube is of the same diameter as that of the tap, the interface can be run to the bottom of the tube, the final drop of dimethyl sulphate being removed with filter paper. Reweigh the funnel and the neutral oil insoluble in dimethyl sulphate. Reserve this oil for Determination of Unsulphonated Residue TP 6.

Calculate the percentage of neutral oil soluble and insoluble in dimethyl sulphate on the basis of neutral oil.

The method may be expected to give an accuracy of ± 2. This should be borne in mind when interpreting the results.

Determination of Distillation Range of Neutral Oil TP 5

(*i*) RECOVERY OF NEUTRAL OIL

REAGENTS

- Sodium hydroxide solution (50 per cent W/W)
- Ether (see Appendix D, p. 62)
- Hydrochloric acid (4 per cent W/W)
- Anhydrous sodium sulphate

APPARATUS

- 2 separating funnels (not less than 2000 ml. capacity)
- 1 Liebig condenser (not less than 30″ water jacket) and adapter
- 1 wide 100 ml. beaker
- 1 1000 ml. conical flask
- 1 separating funnel (1500 ml. capacity)
- 1 splash head with side inlet
- 1 water or steam bath
- 1 thermometer (0—200° C.)
- 1 250 ml. distillation flask
- 1 air condenser (Type 3 B.S. 658, 1936)

METHOD

Transfer to the first large separating funnel approximately 200 ml. of the sample, 1000 ml. distilled water, 50 ml. of the sodium hydroxide solution and 500 ml. of ether. Shake and allow to stand overnight.

Withdraw the alkaline layer into the second separating funnel, and, if an intermediate layer of salted-out soap has formed, transfer this to the 1500 ml. separating funnel.

Extract the alkaline layer with three successive 100 ml. lots of ether. To the intermediate layer (if present) add 500 ml. distilled water and extract with three successive 100 ml. lots of ether.

Unite all the ether extracts in the first separating funnel and wash once with 200 ml. distilled water. Reject this wash water and all ether-extracted alkaline layers.

Wash the combined ether extracts with successive 100 ml. lots of 4 per cent hydrochloric acid until the acid washings are lighter in colour than 0.001N aqueous iodine solution. Carbonaceous sludge, if troublesome, may be filtered off at the pump. Reject all acid washings. Concentrate the ether solution to 400—600 ml. on the water bath, distilling the ether through the water-cooled Liebig condenser. Cool the concentrated ether solution, transfer to a dry flask and shake well with 50 g. anhydrous sodium sulphate. Stand overnight and filter into the 1000 ml. conical flask.

Remove as much ether as possible from the extract by distillation on a water or steam bath, using the long water-cooled Liebig condenser.

Transfer the extract to the 250 ml. distillation flask closed by a cork carrying the thermometer so fitted that the bottom of the capillary is level with the lower edge of the side tube. Attach to the air condenser and heat carefully on a sand bath or hot plate. When vigorous boiling due to the ether has finished, replace the receiver by the wide 100 ml. beaker and continue heating until the extract again boils actively or until the thermometer indicates a temperature of 180° C. When cool, wash through the condenser with the bulk of the neutral oil and to this add the residue obtained by allowing the ether to evaporate from the distillate, in the 100 ml. beaker, for six hours at room temperature.

(*ii*) Distillation of Neutral Oil

Apparatus

Standard distillation apparatus. (*Standard Methods for Testing Tar and its Products*, 2nd Ed. 1938, Serial No. C.O. 3-38, page 270.)

Method

Weigh each of the three receivers. Weigh accurately 100 g. $\pm$ 1 of the neutral oil in the F 4 distillation flask and distil at the steady rate of 5 ml. $\pm$ 0.5 per minute (approximately 3 drops in 2 seconds) into the first receiver. When the thermometer indicates 290° C., remove the receiver and replace by the second receiver; substitute the third receiver as soon as the thermometer indicates 340° C. Remove the third receiver as soon as the thermometer indicates 375° C., at which stage the distillation is stopped. Do not collect the drainings from the condenser with this fraction.

Calculate the percentage by weight of neutral oil which has distilled at each of the above temperatures.

Determination of Unsulphonated Residue of Neutral Oil Insoluble in Dimethyl Sulphate TP 6

(*i*) Determination of Specific Gravity

Apparatus

1 10 ml. British Standard Density Bottle B.S. 733, 1937.

1 water bath at 15.5° C.

METHOD

Fill the tared bottle with distilled water at about 16° C. and place in a water bath maintained at 15.5° C. for 5 minutes. Replace the stopper and wipe the top, remove the bottle from the water bath, wipe the adhering water from the sides of the bottle and weigh. Let Ww be the weight of water required to fill the bottle at 15.5° C. Repeat this procedure using the oil obtained from method TP 4 in place of water. Let W_O be the weight of oil required to fill the bottle at 15.5° C.

$$\text{Specific gravity at } 15.5°\text{C.}/15.5° = \frac{W_O}{W_W}$$

(*ii*) DETERMINATION OF UNSULPHONATED RESIDUE

REAGENTS

Sulphuric acid 98.6 per cent $\pm$ 0.1 H_2SO_4. Sulphuric acid, pure, concentrated, sp. gr. 1.84. (See Appendix E, page 62, for details of preparation and standardization of sulphuric acid).

APPARATUS

2 Fifty per cent 9 gramme Babcock Bottles for Testing Cream, B.S. 755, 1937
1 5 ml. pipette
1 50 ml. burette, graduated in 0.1 ml. divisions
1 water bath, to take 2 test bottles (See Note 1)
A centrifuge capable of rotating test bottles of 165 mm. overall height at 1000-1250 r.p.m. and provided with a protecting cover (See Note 2)

METHOD

Introduce with the pipette about 5 ml. of the neutral oil insoluble in dimethyl sulphate (TP 4) into a tared, thoroughly clean, dry test bottle and weigh. Add slowly from the burette 20 ml. of 98.6 per cent sulphuric acid in four equal portions, washing down any oil remaining in the neck. Shake the bottle rapidly for ten seconds after each addition of acid. Cool if necessary, to keep the temperature below 60° C. Immerse the bottle, lightly stoppered with a rubber bung, in the boiling water bath for one hour, clamping it in a vertical position with the bulb completely submerged. (See Note 1). Remove the bottle from the bath at 10 minute intervals, shake for 10 seconds and replace. Take out the bottle after one hour and add sufficient sulphuric acid, sp. gr. 1.84, to bring the oil into the graduated portion of the neck. Place the bottle in the centrifuge and counterpoise, preferably with the second bottle in which a duplicate determination is being simultaneously carried out. Centrifuge for 5 minutes at 1000-1250 r.p.m. (See Note 2). Take out, cool to 15° C. and read the volume of oil as accurately as possible with the help of a lens (1 division = 0.05 ml.). Centrifuge again, until the volume of oil is constant.

$$\%\ \text{unsulphonated residue v/v} = \frac{\text{vol. of oil read} \times \text{sp. gr. of oil taken} \times 100}{\text{wt. of oil taken}}$$

Notes:

1. An oil bath or steam oven maintained at 98° C. $\pm$ 2 may be used in place of the water bath.
2. Centrifuges with lower speeds can be used, but the period of rotation may have to be increased, until a constant reading of the volume of oil is obtained.
3. If the unsulphonated oil layer is so dark that the line of demarcation between oil and acid is not clearly visible, a few drops of water should be added to form an intermediate layer, when the volume can be read after a few minutes' standing. This procedure tends to give slightly higher results.
4. Duplicate results should agree within 2 per cent, based on the neutral oil.
5. The sulphuric acid reagent should be carefully standardized, as slight variations in strength from 98.6 per cent affect the result substantially. The strength of the acid should be checked not more than 24 hours before each determination is carried out (See Appendix E, p. 62).

Determination of Stability of Undiluted Wash TP 7

APPARATUS

A refrigerator maintained at − 5° C. ± 1 *or* a large vacuum flask
1 1500 ml. beaker 1 water bath
1 8 oz. white glass bottle *or* 1 wide necked 4 oz. white glass bottle

METHOD

(a) *Miscible Tar-Petroleum Oil Winter Washes*

Place 200 ml. of the sample, contained in the well-corked 8 oz. white glass bottle, in the refrigerator at − 5° C. ± 1 for 48 hours; *or* place the 8 oz. bottle containing 200 ml. of the sample in the centre of the vacuum flask surrounded by a freezing mixture capable of maintaining the temperature at − 5° C. ± 1 (See Appendix C, p. 62).

After 48 hours examine the cooled sample for cloudiness.

Warm to 0° C. and, without avoidable agitation, decant rapidly 75 ml. of the sample into 925 ml. of ice-cooled distilled water in the 1500 ml. beaker, stirring the water vigorously. Allow to stand for 4 hours at room temperature.

Note the amount of oil separated.

The sample shall be considered to comply with the specification if

(*i*) after cooling, the undiluted wash shows no marked cloudiness; and

(*ii*) after standing at room temperature, the diluted wash shows not more than slight traces of oil separation.

(b) *Stock Emulsion Tar-Petroleum Oil Winter Washes*

Place 75 ml. of the sample contained in the well-corked 4 oz. white glass bottle in the refrigerator at − 5° C. ± 1 for 48 hours; *or* place the 4 oz. bottle, containing 75 ml. of the sample, in the centre of the vacuum flask surrounded by a freezing mixture capable of maintaining the temperature at − 5° C. ± 1. (See Appendix C, p. 62).

After 48 hours examine the cooled sample for separation of free oil.

Place the bottle in the water bath at 20° C. ± 3 for one hour. Pour the contents into 825 ml. of distilled water at room temperature with vigorous stirring. Remove as much residual emulsion as possible from the bottle by rinsing with a further 100 ml. of distilled water at room temperature, adding to the main bulk and maintaining the stirring during this operation. Allow to stand for 4 hours at room temperature.

Note the amount of oil separated.

The sample shall be considered to comply with the specification if

(*i*) after cooling, the undiluted wash shows no obvious separation of oil; and

(*ii*) after standing at room temperature, the diluted wash shows not more than slight traces of oil separation.

Determination of Stability of Diluted Wash TP 8

REAGENT

Dissolve 1.85 g. of calcium carbonate (A.R.) and 0.74 g. of magnesium oxide (A.R) in the minimum of dilute hydrochloric acid.

Expel the excess acid by evaporation to dryness on a water bath and dissolve the residue in 100 ml. of water.

APPARATUS

1 1500 ml. beaker

METHOD

(a) *Miscible Tar-Petroleum Oil Winter Washes*

To 890 ml. of distilled water at room temperature add 10 ml. of the stock solution of calcium and magnesium chlorides. This, when the sample is added, will give a solution containing calcium and magnesium chlorides in equimolecular proportions together equivalent to 40 parts of calcium carbonate per 100,000. Stir vigorously with a glass rod, add rapidly 100 ml. of the sample at room temperature. Allow to stand for 4 hours. Note the free oil separated.

The sample shall be considered to comply with the specification if not more than slight traces of free oil have separated.

(b) *Stock Emulsion Tar-Petroleum Oil Winter Washes*

To 790 ml. of distilled water at room temperature add 10 ml. of the stock solution of calcium and magnesium chlorides. This, when the sample is added, will give a solution containing calcium and magnesium chlorides in equimolecular proportions together equivalent to 40 parts of calcium carbonate per 100,000. Add 100 ml. of the sample to 100 ml. of the prepared hard water and mix thoroughly. Add the mixture rapidly to the remaining hard water at room temperature, stirring vigorously with a glass rod. Allow to stand for 4 hours. Note the amount of free oil separated.

The sample shall be considered to comply with the specification if not more than slight traces of free oil have separated.

DINITRO-*ORTHO*-CRESOL-PETROLEUM OIL WINTER WASHES

SPECIFICATION

The specification refers to polyphase products compounded from petroleum oils and dinitro-*ortho*-cresol (2:4-dinitro-6-methyl-phenol or 3:5-dinitro-*ortho*-cresol) referred to as DNC.

1. *Content of Neutral Oil*

The wash shall yield not less than 60 per cent by weight neutral oil when analysed by the prescribed method DNC 2 or DNC 2a.

2. *Specific Gravity*

The specific gravity of the isolated neutral oil shall be between 0.86 and 0.93 at 15.5° C./15.5° when determined by the prescribed method DNC 4.

3. *Volatility*

The amount of isolated neutral oil distilling at an oil temperature of 350° C. shall be not more than 5 per cent of its volume when determined by the prescribed method DNC 5.

4. *Unsulphonated Residue*

Not less than 65 per cent by volume of the total neutral oil shall remain unsulphonated when treated in the prescribed manner DNC 6.

5. *Content of Dinitro-ortho-cresol*

The content of dinitro-*ortho*-cresol, when determined by the prescribed method (DNC 7) and expressed as per cent by weight of the product shall be not less than 1/45th of the weight of neutral oil in the product.

6. *Stability*

(*a*) The undiluted wash shall conform to the prescribed test for stability DNC 8.

(*b*) The diluted wash shall conform to the prescribed test for stability DNC 9.

Note. Only emulsifying agents at present in common use in Great Britain have been taken into consideration. If new emulsifiers are introduced, it may be necessary at some future date to review the specification and methods of analysis.

METHODS OF ANALYSIS

Sampling DNC 1

The method of sampling will depend upon the circumstances and is to be based on *Standard Methods for Testing Petroleum and its Products*, 9th Ed., 1948, page 344 *et seq.* The manufacturer's instructions, if any, for diluting the product should accompany the sample, which should not be less than one quart in volume. Samples must be placed in glass containers and the colour of the product at the time of sampling noted on the label. DNC is susceptible to reduction in certain circumstances and a red or brownish-red colour may indicate chemical instability of the product.

Determination of Neutral Oil Content

The method (DNC 2 or DNC 2a) to be used is determined by the presence or absence of reducing substances in the product. Their presence is detected by the formation of red cuprous oxide when a little of the product is warmed with twice its volume of Fehling's solution. If no cuprous oxide is produced, Method DNC 2 is to be used, otherwise Method DNC 2a is to be used.

METHOD DNC 2

REAGENTS

Sodium hydroxide solution (10 per cent W/W)
Sodium hydroxide solution (1 per cent W/W)
Ether (see Appendix D, p. 62)
Sodium chloride solution (saturated)
Anhydrous sodium sulphate
Hydrochloric acid solution (4 per cent W/W)
Sulphuric acid solution (50 per cent V/V)

APPARATUS

2 1500 ml. separating funnels
1 250 ml. separating funnel
1 filter funnel
1 Liebig condenser (not less than 30″ water jacket) and adapter
1 1000 ml. lipped beaker
1 2000 ml. conical flask
1 1500 ml. conical flask
1 200 ml. extraction flask
1 wash bottle of dry ether
1 splash head with side inlet
1 water or steam bath
1 water or steam oven at 98° C.±2
1 desiccator
1 ground glass plate
1 1000 ml. round-bottomed steam distillation flask

METHOD

Weigh accurately about 50 ml. of the well-stirred sample. Wash into the 1500 ml. separating funnel with 500 ml. of water. Add 100 ml. of 10 per cent sodium hydroxide solution and 500 ml. of ether. Shake and allow to stand until a clear ether layer has separated. If the emulsion has not broken sufficiently after standing overnight, add 10 ml., or more if necessary, of saturated sodium chloride solution and rotate gently until the emulsion breaks.

Certain emulsions are not completely broken after a short period by this alkaline treatment. A partial separation of either the ether or the aqueous layer is obtained. By withdrawing the clear phase and replacing with water or ether, according to the phase removed, a complete separation is eventually obtained.

Withdraw the lower layer into the second 1500 ml. separating funnel and to this add 200 ml. of ether and shake. After allowing to stand for one hour, withdraw the lower layer into the lipped beaker and add the ether layer to that from the first extraction which remains in the first separating funnel.

Return the alkaline layer to the empty separating funnel and repeat its extraction with 200 ml. lots of ether, until a drop of the ether washings when allowed to evaporate from the cleaned ground glass plate no longer leaves a continuous film of oil. Add the ether washings to the first separating funnel and wash three times with successive 50 ml. lots of 1 per cent sodium hydroxide solution. Wash once with 100 ml. of distilled water. Combine the washings and extract once with 200 ml. of ether. Discard the ether layer.

Transfer the washings and the alkaline layer in the lipped beaker to the round-bottomed steam distillation flask and acidify with slight excess of the sulphuric acid solution (about 30 ml. are required). Reserve for the determination of DNC content (DNC 7).

Wash the combined ether layers once with 100 ml. of 4 per cent hydrochloric acid. Transfer the acid layer to the 250 ml. separating funnel and wash twice with 50 ml. lots of ether. Reject the acid layer.

Add the ether washings to the main bulk of the ether extract in the first separating funnel and wash once with 100 ml. of water. Reject the aqueous washings. Transfer the ether solution to the large conical flask and concentrate to 250-300 ml. on the water bath, distilling the ether through the water-cooled Liebig condenser. When cool, transfer to a dry flask, shake well with 20 g. of anhydrous sodium sulphate and allow to stand overnight.

Filter the ether solution through an open-textured filter paper, collecting the first 100 ml. of the filtrate in the tared extraction flask and the remainder in another flask. Transfer the residual sodium sulphate from the conical flask to the filter paper by means of successive 50 ml. lots of ether (previously dried over anhydrous sodium sulphate) and finally wash the residue and filter paper with dry ether from a wash bottle until a drop of the ether washings, when allowed to evaporate from the cleaned ground glass plate no longer leaves a continuous film of oil.

Distil the ether from the first 100 ml. of the filtrate on the water or steam bath, using the water-cooled Liebig condenser to which the extraction flask is attached by way of the splash head. Add the combined washings and remainder of the filtrate to the residue in the extraction flask at suitable stages. This may be done, if convenient, by means of a suitable separating funnel, the delivery tube of which is inserted through the cork of the extraction flask.

Remove the last traces of ether by heating the flask in the oven at 98° C. $\pm$ 2 to constant weight, displacing the ether vapour by a puff of air from the bellows at intervals.

Transfer the flask to the desiccator, reweigh when cool, and calculate the percentage (W/W) of neutral oil in the wash.

The method may be expected to give an accuracy of $\pm$ 2. This should be borne in mind when interpreting the results.

METHOD DNC 2a

Reagents

Sulphuric acid solution (5 per cent V/V)
Sulphuric acid solution (50 per cent V/V)
Sodium hydroxide solution (10 per cent W/W)
Cetyl pyridinium bromide solution (see Appendix F, p. 63)
Anhydrous sodium sulphate
Ether (see Appendix D, p. 62)

Apparatus

2 1500 ml. separating funnels
1 1500 ml. conical flask
1 1000 ml. conical flask
1 1000 ml. round-bottomed steam distillation flask
1 200 ml. extraction flask
1 splash head with side inlet
1 filter funnel
1 water or steam bath
1 water or steam oven at 98° C. ± 2
1 desiccator
1 Liebig condenser (not less than 30″ water jacket) and adapter
1 ground glass plate

Method

Weigh accurately about 100 ml. of the well-stirred sample. Wash into the 1500 ml. separating funnel with about 400 ml. water, followed by 400 ml. ether and 50 ml. 5 per cent sulphuric acid. Shake. Add the 5 per cent cetyl pyridinium bromide solution, *2 ml. at a time,* shaking after each addition until the emulsion breaks cleanly and quickly. Withdraw the aqueous layer. Filter the ether layer into the dry 1500 ml. flask. Return the aqueous layer to the separating funnel and re-extract with 200 ml. lots of ether, filtering the ether extracts as before. Repeat the ether extraction until a drop of the extract, when allowed to evaporate from filter paper, leaves no yellow stain. (Usually three extractions are required.) Discard the aqueous layer. Wash the filter and filter paper with ether until colourless when dry. Unite all ether extracts and washings in the 1500 ml. conical flask and concentrate to about 400 ml. on the water bath, distilling the ether through the water-cooled Liebig condenser.

Transfer the ether solution, when cool, to the second separating funnel, add about 400 ml. water and 30 ml. sodium hydroxide solution and shake. Withdraw the aqueous layer and wash the ether layer with further quantities of 50 ml. water until the washings are colourless. Withdraw the ether solution. Return the aqueous washings to the separating funnel and extract once with 200 ml. ether. Withdraw the aqueous layer and wash the ether extract remaining in the funnel with further 50 ml. lots of water until the washings are colourless.

Unite all aqueous solutions and washings, transfer to the round-bottomed steam distillation flask and acidify with 20 ml. 50 per cent sulphuric acid. (It is necessary to complete the extraction of the cresol and its recovery by acidification as speedily as possible to lessen the chances of its reduction in the alkaline phase.) Reserve this acidified solution for the determination of DNC content, DNC 7.

Transfer the ether solution and washings to the 1000 ml. conical flask and concentrate to 250-300 ml. on the water bath, distilling the ether through the water-cooled Liebig condenser. When cool, transfer to a dry flask, shake well with 20 g. anhydrous sodium sulphate and allow to stand overnight.

Filter the ether solution through an open-textured filter paper, collecting the first 100 ml. of the filtrate in the tared extraction flask and the remainder in another flask. Transfer the residual sodium sulphate from the conical

flask to the filter paper by means of successive 50 ml. lots of ether (previously dried over anhydrous sodium sulphate) and finally wash the residue and filter paper with dry ether from a wash bottle until a drop of the ether washings, when allowed to evaporate from the cleaned ground glass plate, no longer leaves a continuous film of oil.

Distil the ether from the first 100 ml. of the filtrate on the water or steam bath, using the water-cooled Liebig condenser to which the extraction flask is attached by way of the splash head. Add the combined washings and remainder of the filtrate to the residue in the extraction flask at suitable stages. This may be done, if convenient, by means of a suitable separating funnel, the delivery tube of which is inserted through the cork of the extraction flask.

Remove the last traces of ether by heating the flask in the oven at 98° C. ± 2 to constant weight, displacing the ether vapour by a puff of air from the bellows at intervals.

Transfer the flask to the desiccator, reweigh when cool, and calculate the percentage (W/W) of neutral oil in the wash.

The method may be expected to give an accuracy of ±2. This should be borne in mind when interpreting the results.

Recovery of Neutral Oil for Analysis DNC 3

Note. This recovery will not be necessary if Method DNC 2 or DNC 2a has yielded sufficient neutral oil for Methods DNC 4, 5 (a) and 6.

Reagents

- Sodium hydroxide solution (50 per cent W/W)
- Hydrochloric acid (4 per cent W/W)
- Ether (see Appendix D, p. 62)
- Anhydrous sodium sulphate
- Sodium chloride solution (saturated)

Apparatus

- 2 separating funnels (not less than 2000 ml. capacity)
- 1 250 ml. separating funnel
- 1 Liebig condenser (not less than 30″ water jacket) and adapter
- 1 wide 100 ml. beaker
- 1 splash head with side inlet
- 2 1000 ml. conical flasks
- 1 water or steam bath
- 1 thermometer (0-200° C.)
- 1 500 ml. distillation flask
- 1 air condenser (type 3, B.S. 658, 1936)

Method

Transfer to the first large separating funnel approximately 300 ml. of the sample, 1000 ml. of distilled water and 500 ml. of ether. Add at least 10 ml. of the sodium hydroxide solution and, if necessary, saturated sodium chloride solution in amounts found by previous experience (under Method DNC 2) to be required to break the emulsion.

When a satisfactory separation of aqueous and ether layers has been obtained, transfer the aqueous layer to the second separating funnel and extract with three successive 200 ml. lots of ether.

Unite all the ether extracts in the first separating funnel and wash once with 200 ml. of distilled water. Reject this wash water and all ether extracted alkaline layers.

Wash the combined ether layers once with 100 ml. of 4 per cent hydrochloric acid. Transfer the acid layer to the 250 ml. separating funnel and wash twice with 50 ml. lots of ether. Reject the acid layer.

Add the ether washings to the main bulk of the ether extracts in the first separating funnel and wash once with 100 ml. of water. Reject the aqueous washings. Concentrate the ether solution to 400-600 ml. on the water bath, distilling the ether through the water-cooled Liebig condenser. Cool the concentrated ether solution, transfer to a dry flask and shake well with 50 g. of anhydrous sodium sulphate. Stand overnight and filter into the 1000 ml. conical flask.

Remove as much ether as possible from the extract by distillation on a water or steam bath, using the water-cooled Liebig condenser.

Transfer the extract to the 500 ml. distillation flask and close by a cork carrying the thermometer, so fitted that the bottom of the capillary is level with the lower edge of the side tube. Attach to the air condenser and heat carefully on a sand bath or hot plate. When vigorous boiling due to the ether has finished, replace the receiver by the wide 100 ml. beaker and continue heating until the extract again boils actively or until the thermometer indicates a temperature of 180° C. When cool, wash through the condenser with the bulk of the neutral oil and to this oil add any residue obtained by allowing the ether to evaporate from the distillate, in the 100 ml. beaker, for at least six hours at room temperature.

Determination of Specific Gravity of Neutral Oil DNC 4

APPARATUS

1 10 ml. British Standard Density Bottle B.S. 733, 1937

1 water bath at 15.5° C.

METHOD

Fill the tared bottle with distilled water at about 16° C. and place for 5 minutes in a water bath maintained at 15.5° C. Replace the stopper, wipe top and remove the bottle from the water bath, wipe the adhering water from the sides of the bottle and weigh. Let W_W be the weight of water required to fill the bottle at 15.5° C. Repeat this procedure using the neutral oil in place of water. Let W_O be the weight of oil required to fill the bottle at 15.5° C.

$$\text{Specific gravity at } 15.5°\text{C.}/15.5° = \frac{W_O}{W_W}$$

Determination of Volatility of Neutral Oil DNC 5

APPARATUS

A standard distillation flask (Schedule F4, *Standard Methods for Testing Tar and its Products*, S.T.P.T.C. 2nd Ed. 1938, p. 365), held in a vertical position by a clamp at the extreme upper end of the neck

A standard thermometer having a range of 90° to 400° C. (Schedule No. T4a—S.T.P.T.C.)

A standard draught screen (Schedule No. S3—S.T.P.T.C.) from which the shelf has been removed

A standard air condenser (Schedule No. C3—S.T.P.T.C.). The side arm of the flask shall extend at least 25 mm. beyond the cork in the upper end of the condenser

1 100 ml. Crow receiver

2″ length of thin-walled capillary tubing (as used for melting point determinations)

METHOD

(a) *Preliminary Examination*

Transfer to the distillation flask 25 ml. neutral oil, add the short length of capillary tubing and replace the flask in position in the apparatus.

Fit the thermometer by means of a cork into the neck of the flask so that the mercury bulb is just clear of the bottom of the flask.

Using the naked flame of the burner, heat the oil so that the temperature recorded by the thermometer increases, above 250° C., at a rate of 5° C. per 30 seconds ± 10.

Note the number of drops of distillate which fall from the side arm of the flask before the thermometer reads 350° C. If this number is not more than two, the amount of oil distilling at an oil temperature of 350° C. does not exceed 5 per cent by volume. If this number is greater than two, the volatility of the oil must be determined by method (b).

(b) *Full Method*

Recover a sufficient amount of neutral oil by the prescribed method DNC 3 to permit the weighing into the distillation flask of an amount equal to 100 ml. Add the short length of capillary tubing and replace the flask in position in the apparatus.

Fit the thermometer by means of a cork into the neck of the flask so that the mercury bulb is below the surface of the oil, the bottom of the capillary thread being level with that surface.

Using the naked flame of the burner, heat the oil so that the temperature recorded by the thermometer increases, above 250° C., at a rate of 5° C. per 30 seconds ±10.

When the thermometer reads 350° C., remove the Crow receiver and record the volume of distillate collected.

Determination of Unsulphonated Residue of Neutral Oil DNC 6

REAGENTS

Sulphuric acid 98.6 per cent ± 0.1 H_2SO_4 (see Appendix E, p. 62)

Sulphuric acid, pure, concentrated, sp. gr. 1.84.

APPARATUS

2 Fifty per cent 9 gramme Babcock Bottles for Testing Cream, B.S. 755, 1937

1 5 ml. pipette

1 50 ml. burette graduated in 0.1 ml. divisions

1 water bath to take 2 test bottles (see Note 1)

A centrifuge capable of rotating test bottles of 165 mm. overall height at 1000-1250 r.p.m. and provided with a protecting cover and a shield not less than 2 ft. in diameter (see Note 2)

METHOD

Introduce with the pipette about 5 ml. of neutral oil into a tared, thoroughly clean, dry test bottle and weigh. Add slowly from the burette 20 ml. of 98.6 per cent sulphuric acid in four equal portions, washing down any oil remaining in the neck. Shake the bottle rapidly for ten seconds after each addition of acid. Cool, if necessary, to keep the temperature below 60° C. Immerse the bottle, lightly stoppered with a rubber bung, in the boiling water bath for one hour, clamping it in a vertical position with the bulb completely submerged (see Note 1). Remove the bottle from the bath at 10 minute intervals, shake for 10 seconds and replace. Take out the bottle

after 1 hour and add sufficient sulphuric acid, sp. gr. 1.84, to bring the oil into the graduated portion of the neck. Place the bottle in the centrifuge and counterpoise, preferably with the second bottle in which a duplicate determination is being simultaneously carried out. Centrifuge for 5 minutes at 1000-1250 r.p.m. (see Note 2), take out, cool to 15° C. and read the volume of oil as accurately as possible with the help of a lens (1 division = 0.05 ml.). Centrifuge again, until the volume of oil is constant.

$$\% \text{ unsulphonated residue v/v} = \frac{\text{vol. of oil read} \times \text{sp. gr. of oil taken} \times 100}{\text{wt. of oil taken}}$$

Notes:

1. An oil bath or steam oven maintained at 98° C. ± 2 may be used in place of the water bath.

2. Centrifuges with lower speeds can be used, but the period of rotation may have to be increased until a constant reading of the volume of oil is obtained.

3. If the unsulphonated oil layer is so dark that the line of demarcation between oil and acid is not clearly visible, a few drops of water should be added to form an intermediate layer, when the volume can be read after a few minutes' standing. This procedure tends to give slightly higher results.

4. Duplicate results should agree within 2 per cent, based on the neutral oil.

5. The sulphuric acid reagent should be carefully standardized, as slight variations in strength from 98.6 per cent affect the result substantially. The strength of the acid should be checked not more than 24 hours before each determination is carried out.

Determination of Dinitro-*ortho*-Cresol Content DNC 7

Reagents

0.1N Sodium thiosulphate solution (standardized against 0.1N potassium iodate solution)

0.1N Iodine solution (standardized against the thiosulphate solution)

0.5N Iodide-iodate solution (see Appendix G, p. 63)

N Sulphuric acid solution

Anhydrous sodium sulphate

Starch indicator solution

Ether (see Appendix D, p. 62)

Absolute alcohol or rectified spirit

Nitron solution (10 per cent nitron W/V in 4 per cent acetic acid V/V; filter immediately before use)

Saturated sodium chloride solution

Nitron-DNC complex, prepared by method given below, from pure DNC obtained by crystallization of the commercial product from absolute alcohol to sharp and constant melting point.

Apparatus

1 Liebig condenser (not less than 30″ water jacket) and adapter
1 1500 ml. conical flask
1 1500 ml. separating funnel
1 steam generator
1 400 ml. tall beaker
1 25 ml. pipette
2 burettes
1 melting point apparatus
Broken pieces of porous tile
1 splash head with side inlet
1 water or steam bath
1 250 ml. graduated flask
1 350 ml. conical flask
1 sintered glass crucible
1 water or steam oven at 98° C. ±2
1 glass rod fitted with rubber "policeman"
1 watch glass
1 vacuum desiccator containing sulphuric acid or calcium chloride

Methods

Add to the acidified aqueous suspension of DNC contained in the steam distillation flask about 10 g. anhydrous sodium sulphate and a few pieces of porous tile. Connect the flask, provided with a steam tube and an efficient splash head, to the Liebig condenser. Distil over a Bunsen, gently at first, until the dissolved ether is removed, then vigorously until some 200 ml. only remain, collecting the distillate in the 1500 ml. conical flask. Now connect the steam tube to the steam generator and remove residual DNC from the distillation flask by passing a brisk current of steam until the condensate in the splash head is colourless.

Disconnect the condenser and wash any DNC from the tube into the receiver with ether. Transfer the contents of the receiver to the separating funnel, add 20 ml. saturated sodium chloride solution and 2 drops N sulphuric acid, and extract by vigorous shaking with 4 successive 250 ml. lots of ether. Combine the ether extracts in the 1500 ml. conical flask and distil off the ether on the water or steam bath through the water-cooled Liebig condenser.

Transfer the residue to the 250 ml. graduated flask with alcohol and make up to the mark.

Allow a few ml. of the alcoholic solution to evaporate on a watch glass. Place the watch glass in a vacuum desiccator overnight to ensure complete dryness. Take the melting point of the crystalline residue. If the melting point is approximately 86° C. it may be assumed that the residue is substantially DNC and that its estimation is possible by the iodometric and gravimetric methods described below. If the melting point is low, steam volatile acids may be present and the gravimetric method only should be used.

Iodometric Method. Pipette 25 ml. of the alcoholic solution into the 350 ml. conical flask and add 10 ml. of the iodide-iodate solution. Dissolve the potassium salt which crystallizes out, by the addition of water (about 75 ml.) until the solution is clear. Add 20 ml. 0.1N thiosulphate solution and determine the excess by back titration with 0.1N iodine solution, adding starch just before the end-point. If the volume of thiosulphate solution is x ml., the weight of DNC in the aliquot is $0.01981\ (20 - x)$ g.

Gravimetric Method. Pipette 25 ml. of the alcoholic solution into the tall 400 ml. beaker. Heat to boiling on the water bath and add hot water slowly until incipient precipitation of the DNC (about 200 ml. are required). Heat on gauze over a low flame and when boiling add 5 ml. of the filtered nitron solution and stir well with a glass rod fitted with a rubber "policeman." Stand overnight. Filter through a tared sintered glass crucible and wash with about 50 ml. water. Dry in the oven for six hours and reweigh. The weight of DNC in the aliquot is equal to the weight of the complex multiplied by 0.3883.

Each method may be expected to give an accuracy of $\pm$ 0.1 and this should be borne in mind when interpreting the results.

As a check on the assumption that the nitro derivative under examination is DNC, determine the melting point of the complex, attaching alongside the melting point tube on the thermometer a second tube containing authentic nitron-DNC complex. If the upper limit of the melting range of the complex under test is lower by 5° C. or more than that of the authentic complex, the factor 0.3883 is inapplicable and the analytical result is meaningless. In such a case the analyst can confirm that his product is not a pure nitron-DNC complex by determining the mixed melting point with the authentic

complex. If the mixed melting point is higher than that of the suspect nitron-DNC complex, the DNC present in the stock emulsion is probably contaminated with other nitro derivatives; a lower mixed melting point indicates the absence of DNC from the stock emulsion, a different nitro derivative being present.

Determination of Stability of the Undiluted Wash at low temperature DNC 8

APPARATUS

A refrigerator maintained at − 5° C. ± 1 *or* a large vacuum flask.
1 1500 ml. beaker.
1 water bath.
1 wide-necked 4 oz. white glass bottle.

METHOD

Place 75 ml. of the sample contained in the well-corked 4 oz. white glass bottle in the refrigerator at − 5° C. ± 1 for 48 hours, *or* place the 4 oz. bottle, containing 75 ml. of the sample, in the centre of the vacuum flask surrounded by a freezing mixture capable of maintaining the temperature at − 5° C. ± 1 (see Appendix C, p. 62).

After 48 hours, examine the cooled sample for separation of free oil.

Place the bottle in the water bath at 20° C. ± 3 for one hour. Pour the contents into 825 ml. of distilled water at room temperature with vigorous stirring. Remove as much residual emulsion as possible from the bottle by rinsing with a further 100 ml. of distilled water at room temperature, adding to the main bulk and maintaining the stirring during this operation. Allow to stand 4 hours at room temperature.

Note the amount of oil separated.

The sample shall be considered to comply with the specification if

(*i*) after cooling, the undiluted wash shows no obvious separation of oil, and

(*ii*) after standing at room temperature, the diluted wash shows not more than slight traces of oil separation.

Determination of Stability of Diluted Wash DNC 9

REAGENT

Dissolve 1.85 g. of calcium carbonate (A.R.) and 0.74 g. of magnesium oxide (A.R.) in the minimum of dilute hydrochloric acid.

Expel the excess acid by evaporation to dryness on a water bath and dissolve the residue in 100 ml. of water.

APPARATUS

1 1500 ml. beaker.

METHOD

To 940 ml. of distilled water at room temperature add 10 ml. of the above stock solution of calcium and magnesium chlorides. This, when the sample is added, will give a solution containing calcium and magnesium chlorides in equimolecular proportions together equivalent to 40 parts of calcium carbonate per 100,000. Add 50 ml. of the sample to 50 ml. of the prepared hard water and mix thoroughly. Add the mixture rapidly to the remaining hard water at room temperature, stirring vigorously with a glass rod. Allow to stand for 4 hours. Note the amount of free oil separated.

The sample shall be considered to comply with the specification if not more than slight traces of free oil have separated.

APPENDIX

(A) Dimethyl Sulphate

Specification

1. The material shall consist of dimethyl sulphate in the form of a colourless or nearly colourless liquid. It shall be free from suspended matter and visible water.

2. The free acidity of the material shall not exceed 0.5 per cent by weight (calculated as sulphuric acid), when determined by the method described in section (*a*) below.

3. The material shall contain not less than 95 per cent by weight of dimethyl sulphate $(CH_3)_2SO_4$ when determined by the method described in section (*b*) below.

Methods of Analysis

(*a*) Free Acidity

Reagents

N sodium hydroxide solution

0.1 per cent methyl orange solution

Apparatus

1 weighing bottle

1 500 ml. separating funnel

Method

Weigh accurately 10 to 15 g. of the sample (X g.) from the weighing bottle into the 500 ml. separating funnel, add 200 ml. ice-cold water and shake for 1 minute. Allow to settle for 5 minutes, run off as much as possible of the oily layer and *immediately* titrate the aqueous layer in the separating funnel with N sodium hydroxide solution using methyl orange as indicator.

Per cent by weight free acidity (as sulphuric acid) = A = ml. NNaOH × 0.049 × 100/X.

(*b*) Dimethyl Sulphate Content

Reagents

Hydrochloric acid (A.R. 32 per cent W/W)

0.1 per cent methyl orange solution

N sodium hydroxide solution

Apparatus

1 weighing bottle (or Lunge-Rey pipette)

1 500 ml. porcelain basin

1 500 ml. round-bottomed flask

1 reflux condenser

1 water or steam bath

Method

Weigh accurately about 2 g. of the sample (Y g.) from the weighing bottle or Lunge-Rey pipette into the 500 ml. round-bottomed flask containing 200 ml. of distilled water and 20 ml. A.R. hydrochloric acid. Attach the reflux condenser to the flask. Shake well and heat in the boiling water or steam bath for two hours.

Transfer the contents of the flask to the 500 ml. porcelain basin and evaporate on a boiling-water bath until only a small quantity of liquid remains (about 2-3 ml.).

Continue heating on the boiling-water bath for 15 minutes, then add 50 ml. distilled water and again evaporate to 2-3 ml. Add to the residue 50 ml. distilled water and 2-3 drops of 0.1 per cent methyl orange solution, and titrate with N sodium hydroxide solution.

Per cent by weight dimethyl sulphate (uncorrected for free acidity) = B = ml. N NaOH × 0.06305 × 100/Y.

Per cent by weight dimethyl sulphate (corrected for free acidity) = B − 1.286 A, where A = per cent by weight free acidity calculated as sulphuric acid.

(B) Preparation of Freezing Mixture at − 10° C. ± 1°

The following procedure gives satisfactory results with a vacuum flask of 1 gallon capacity:

Prepare 1-2 litres of a solution containing 20-21 per cent by weight of potassium chloride. Pour this into a suitable vessel and immerse it in a pail containing a freezing mixture prepared by intimately mixing 4.5 kg. of finely pulverized ice and 1.5 kg. of salt. A suitable vessel is a tin (with handle attached) of such diameter that it can be freely lowered into the vacuum flask. Insert the 8 oz. bottle containing 200 ml. of the sample into the potassium chloride solution. Keep the solution in the freezing mixture for some hours, with occasional stirring, until crystallization of the cryohydrate takes place. Transfer the vessel to the vacuum flask and allow to stand for 16 hours. (*Note.* A 20.03 per cent solution of potassium chloride has a cryohydric point of − 11.4° C. A temperature of − 10° C. to − 11° C. will be maintained in the vacuum flask so long as crystals of the cryohydrate remain in the solution. It is therefore necessary to ensure that sufficient cryohydrate crystallizes initially to maintain the required temperature for 16 hours.) The apparatus should be standardized before use, by taking temperature readings under the specified conditions. The potassium chloride solution can be reserved for future use.

(C) Preparation of Freezing Mixture at − 5° C. ± 1°

The following procedure gives satisfactory results with a vacuum flask of 1 gallon capacity:

Place into the vacuum flask 3 kg. of finely pulverized ice. Add 177 ml. of concentrated hydrochloric acid and stir thoroughly. The temperature sinks rapidly to about − 8° C. but on continued stirring will reach equilibrium at about − 6° C. and can be adjusted to − 6° C. by the addition of hydrochloric acid or ice. Pre-cool the 4 oz. bottle containing the wash in ice or in more of the freezing mixture for half an hour before placing in the vacuum flask. Examine the temperature of the mixture in the vacuum flask from time to time and readjust as necessary by the addition of more hydrochloric acid. Each 33 ml. brings down the temperature by about 1° C. Using the quantities suggested, a temperature of − 5° C. ±1° can be maintained for 48 hours.

(D) Ether

Ether of specific gravity 0.730 or less should be employed in the determinations. The ether must be free from impurities likely to interfere with these determinations, and, if necessary, should be distilled before use, preferably over sodium.

(E) Preparation and Standardization of Sulphuric Acid Reagent (98.6 per cent. ± 0.1H_2SO_4)

1. Heat about 70 g. of anhydrous sodium carbonate (A.R.) in a nickel or platinum dish to 200-250° C. for 30 minutes. Cool in a desiccator. Weigh out accurately 53.002 g. of the dried sodium carbonate in a 200 ml. beaker and dissolve in distilled water. Transfer the solution to a 1000 ml. graduated flask and make up to volume.

2. Mix 340 ml. of fuming sulphuric acid (20 per cent free SO_3) with 660 ml. of concentrated sulphuric acid (sp. gr. 1.84) in a stoppered 1000 ml. cylinder. Stopper firmly and shake.

3. Introduce about 5 ml. of the mixed acids into a dry weighing bottle, taking care not to wet the ground glass joint with the acid, stopper and weigh. With a graduated dropping tube withdraw 1 ml. of the acid into a funnel resting in a 500 ml. clean conical flask. Stopper the weighing bottle and reweigh immediately. Let the weight of acid withdrawn $= x$ g.

4. Remove the rubber bulb from the dropping tube and wash the acid into the conical flask with about 150 ml. of distilled water. Add 2 drops of 0.1 per cent methyl orange solution.

5. To 200 ml. of water in a similar conical flask add 2 drops of methyl orange solution and 1 ml. of 0.01N sulphuric acid.

6. Titrate the sulphuric acid (par. 4) with the standard sodium carbonate (par. 1), until the colour exactly matches that in the second flask (par. 5). It may be convenient to over-shoot the end point by about 1 ml. and to titrate back with N sulphuric acid. Let the volume of sodium carbonate solution used $= y$ ml.

$$\text{Strength of sulphuric acid} = \frac{y}{x} \times 4.904 \text{ per cent } H_2SO_4$$

7. Adjust the strength of the acid to 98.6 per cent ± 0.1 H_2SO_4 by the addition of standardized concentrated sulphuric acid and restandardize.

(F) Cetyl Pyridinium Bromide Solution

This solution is conveniently prepared by dissolving 5 g. "Fixanol" (I.C.I. Ltd.) in 100 ml. hot water and filtering. Solutions of any amphipathic substance in which the non-polar hydrophobic group is contained in the cation, e.g. cetyl trimethyl ammonium bromide, and which precipitate emulsifiers such as the lignosulphonates from acid solution, may be substituted for this solution.

(G) 0.5N Iodide-iodate Solution

Dissolve 17.835 g. potassium iodate and 70 g. potassium iodide in distilled water and make up to 1 litre; immediately before use treat this solution with 0.1N thiosulphate, drop by drop, until colourless.

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